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On the steady state fractionation of multicomponent and complex mixtures in an ideal cascade

Part VI—The effect of variations of the relative volatilities, the flow rates and the plate efficiencies

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Abstract—An approximate yet standard procedure, the perturbation method, is used to solve analytically the equation for the steafiy state fractionation of multicomponent and complex mixtures in non-ideal cascades. It is shown that the formulae are easily adaptable to numerical evaluation. The perturbation method is particularly useful when the calculations for a system which is close to ideal must be made. The perturbation method may be considered as a non-ideality superimposed on the ideal solution. The ideal solution may be thought of as the first approximation to the solution while the perturbation is the second approximation. Higher order approximations are difficult to carry out.

Résumé—Pour résoudre analytiquement l'équation relative à la distillation continue de mélanges à composants multiples et complexes, les auteurs utilisent la méthode de perturbation, méthode classique, bien qu'approchée.

La méthode de perturbation s'adapte parfaitement aux évaluations numériques : elle est particulièrement utile quand on étudie un système assimilable à un système idéal. Elle peut être considérée comme une correction d'état réel sur l'hypothèse de la solution idéale. La solution idéale correspond à une approximation du premier ordre et la perturbation à une approximation du second ordre. Il es difficile d'utiliser des approximations d'ordre plus élevé.

1. INTRODUCTION

In this series of articles only ideal cascades with constant relative volatilities and constant molal overflows were considered, with the exception of Part V, where the separation of multicomponent and complex mixtures in a packed column was investigated. It is found, however, that in many instances the mathematical model employed so far is too inadequate to represent the actual physical system, and that therefore, the variations in the relative volatilities of the various components, the unequal molal overflow from plate to plate, and the efficiency of the plates must be taken into account. If this is done, though the resulting equations become badly non-linear and, as consequence, they cannot be solved analytically and have been treated in the past only by the laborious trial and error plate-by-plate procedure, which becomes especially involved as the number of the components in the mixture to be separated becomes large.

It is desired here to present a method by which the equations of such " non-ideal " models could be solved analytically. The method is only approximate and would be expected to be reliable only where the deviations from the norm, or

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ideal, are relatively small; but, in any case, the information obtained from these more realistic models should prove of value in the difficult task of predicting the behaviour of real systems.

In this article, only variations in the relative volatilities and the flow rates with the plate number will be considered. However, the method can readily be extended to cases where Murphree plate efficiencies must be taken into account [1].

2. The Ideal Column with Variable Relative Volatilities and Unequal Molal Overflow. The Basic Equations for the Rectification of Discrete Mixtures*

The basic equation for the enriching section of such a model has already been derived in Part I of this series, and is

$$y_{n+1}(i) = \frac{R_n}{1+R_n}\frac{p_n(i)\,y_n(i)}{\sum p_n(i)\,y_n(i)} + \frac{x_0(i)}{1+R_n} \qquad (1)$$

Now, strictly speaking, R_n and $p_n(i)$ are explicit functions not of n, but of the temperature and the composition of the liquid mixture in each stage. It is proposed, however, to circumvent this difficulty in the following manner. First of all, the model described earlier, that is, in which $R_n = R$ and $p_n(i) = p(i)$, is completely solved, so that the temperature and liquid composition on each plate can be estimated. From this knowledge then, it is possible to construct, approximate to be sure but quite often reliable, functions R_n and $p_n(i)$. It will be assumed therefore that R_n and $p_n(i)$ are known functions.

Equation (1) can now be linearized, as was done in Part I, by a change in the dependent variable. A new function $X_n(i)$ is then defined so that

$$p_n(i)\,y_n(i) = \frac{1}{R_{n-1}+1}\frac{x_0(i)\,X_n(i)}{\sum x_0(i)\,X_{n-1}(i)} \qquad (2)$$

and therefore

$$X_{n+1}(i) = R_n p_{n+1}(i)\,X_n(i) + p_{n+1}(i)\sum_j x_0(j)\,X_n(j) \qquad (3)$$

or, symbolically,

$$X_{n+1}(i) = H_n\,X_n(i) \qquad (4)$$

where H_n is a linear operator. Equation (4) can of course be immediately solved by iteration; however, since an analytic solution presents many advantages, Equation (4) will be solved by an approximate yet standard procedure known as the perturbation method. This discussion will be limited only to the first-order perturbation, since, from the practical computational standpoint, the method rapidly loses any advantage if the pertubation is carried out much further.

It is assumed then, that $X_n(i)$, and H_n are both functions of a certain parameter z, which, in some way, gives a measure of the magnitude of the perturbation, and that the problem has already been solved for the unperturbed case, i.e. when $z = 0$. $X_n(i)$ and H_n are next expanded in powers of z, so that

$$X_n(i) = \overset{\circ}{X}_n(i) + z\,\overset{1}{X}_n(i) + z^2\,\overset{2}{X}_n(i) + \cdots \qquad (5)$$

and

$$H = \overset{\circ}{H} + z\,\overset{1}{H} + z^2\,\overset{2}{H} + \cdots \qquad (5a)$$

If both the above expressions converge, they can be substituted into Equation (4), so that, after equating like powers of z,

$$\overset{j}{X}_n(i) = \sum_{k=0}^{j} \overset{k}{H}\,\overset{j-k}{X}_n(i) \qquad (5b)$$

The method of solving Equation (4) then consists of solving the unperturbed problem, and, by applying (5b) repeatedly with $j = 1, 2, \ldots$, of obtaining the functions $\overset{1}{X}_n(i)$, $\overset{2}{X}_n(i)$, etc. In this article however, only the first two terms in Equation (5) and (5a) will be taken into account.

Let then, with $z = 1$,

$$p_n(i) \equiv \overset{\circ}{p}(i) + \overset{1}{p}_n(i)$$

$$R_n \equiv \overset{\circ}{R} + \overset{1}{R}_n \qquad (6)$$

$$x_0(i) \equiv \overset{\circ}{x}_0 + \overset{1}{x}_0(i)$$

and $\quad R_0 = \overset{\circ}{R}$

* Notation is the same as in Parts I-IV.

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It is supposed, moreover, that the perturbation terms $\overset{1}{p}_n(i)$, $\overset{1}{R}_n$ and $\overset{1}{x}_0(i)$ are small compared to the unperturbed terms. Now since,

$$\overset{1}{H} = \overset{0}{R}\,\overset{1}{p}_{n+1}(i) + \overset{1}{R}_n\,\overset{0}{p}(i) + \overset{1}{p}_{n+1}(i)\sum_j \overset{0}{x}_0(j) + \overset{0}{p}(i)\sum_j \overset{1}{x}_0(j)$$

it follows from Equation (5b), with $j = 1$, that

$$\overline{X}_{n+1}(i) = \overset{0}{H}\,\overline{X}_n(i) + \overset{0}{R}\,\overset{1}{p}_{n+1}(i)\,\overset{0}{X}_n(i) + \overset{1}{R}_n\overset{0}{p}(i)\,\overset{1}{X}_n(i) + \overset{1}{p}_{n+1}(i)\sum_j \overset{0}{x}_0(j)\,\overset{0}{X}_n(j) + \overset{0}{p}(i)\sum_j \overset{1}{x}_0(j)\,\overset{0}{X}_n(j)$$

or

$$\overline{X}_{n+1}(i) = \overset{0}{H}\,\overline{X}_n(i) + F_n(i) + \overset{0}{p}(i)\,f_n \qquad (7)$$

where

$$\overline{X}_n(i) \equiv \overset{0}{X}_n(i) + \overset{1}{X}_n(i) \qquad (7a)$$

and

$$f_n \equiv \sum_j \overset{1}{x}_0(j)\,\overset{0}{X}(j) \qquad (7b)$$

Of course, $F_n(i)$ is a known function, because $\overset{0}{X}_0(i)$, is the solution to the unperturbed problem and is given by Equation (3·6) of Part I with $R = \overset{0}{R}$ and $p(i) = \overset{0}{p}(i)$. Similarly, f_n is known if $\overset{1}{x}_0(i)$ is assumed *a priori*.

Equation (7) is now a non-homogenious partial integrodifference equation which can readily be solved. It was in Part I that the eigenfunctions of the operator $\overset{0}{H}$, that is the functions $v_k(i)$, were defined by Equations (3·7) and (3·8) – again of course with $x_0(i) = \overset{0}{x}_0(i)$, $p(i) = \overset{0}{p}(i)$ and $R = \overset{0}{R}$. Therefore, if

$$\overline{X}_n(i) = \sum_k C_k(n)\,(\overset{0}{R}\lambda_k)^{n-1}\,v_k(i) \qquad (8)$$

and

$$F_n(i) = \sum_k Q_k(n)\,v_k(i) \qquad (8a)$$

it follows, from the orthogonality of the eigenfunctions $v_k(i)$ and Equation (7), that

$$C_k(n+1) = C_k(n) + \frac{Q_k(n) + \overset{0}{R}f_n}{(\overset{0}{R}\lambda_k)^n} \qquad (9)$$

from which it is found that

$$C_k(n) = \sum_{j=1}^{n-1} \frac{Q_k(j) + \overset{0}{R}f_j}{(\overset{0}{R}\lambda_k)^j} + C_k(1) \qquad (10)$$

Finally, since from Equation (3·3) of Part I

$$\overline{X}_1(i) = \frac{\overset{0}{p}(i) + \overset{1}{p}_1(i)}{\overset{0}{R}} \qquad (11)$$

$$C_k(1)\sum_j \frac{\overset{0}{p}(j)\,\overset{0}{x}_0(j)}{(\lambda_k - \overset{0}{p}(j))^2} = 1 + \frac{1}{\overset{0}{R}}\sum_j \frac{\overset{1}{p}_1(j)\,\overset{0}{x}_0(j)}{\lambda_k - \overset{0}{p}(j)} \qquad (12)$$

It must be kept in mind of course, that the function $\overset{0}{x}_0(i)$ and the characteristic numbers λ_k are known, once the unperturbed problem has been completely solved. So, the only unknown in the solution is the function $\overset{1}{x}_0(i)$, which enters into f_n, and which would have to be determined from the feed plate matching equation. This however can easily be accomplished by a method of successive approximations.

A very useful asymptotic expression can be obtained if $x_0(i)$, for some i, is small. Then, compare Equations (3·21)-(3·24), if

$$\overset{0}{w}(i) \equiv R - \sum_j \frac{\overset{0}{p}(j)\,\overset{0}{x}_0(j)}{\overset{0}{p}(i) - \overset{0}{p}(j)} \qquad (13)$$

and

$$\frac{\overset{0}{p}(i)\,\overset{0}{x}_0(i)}{\overset{0}{w}(i)}\left(-\frac{\partial\,\overset{0}{w}(i)}{\partial\,\overset{0}{p}(i)}\right) \ll \overset{0}{w}(i)$$

then

$$\lambda_i - \overset{0}{p}(i) = \frac{\overset{0}{p}(i)\,\overset{0}{x}_0(i)}{\overset{0}{w}(i)}$$

and

$$\sum_j \frac{\overset{0}{p}(j)\,\overset{0}{x}_0(j)}{(\lambda_i - \overset{0}{p}(j))^2} = \frac{[\overset{0}{w}(i)]^2}{\overset{0}{p}(i)\,\overset{0}{x}_0(i)}$$

Therefore, if $x_0(i)$ is sufficiently small

$$\overline{X}_0(i) = C_i(n)\,(\overset{\circ}{R}\,\lambda_i)^{n-1}\,\frac{\overset{\circ}{w}(i)}{\overset{\circ}{x}_0(i)} \tag{14}$$

Naturally, entirely analogous formulae and asymptotic expressions can be obtained for the stripping section, but the details will be omitted here.

The advantage then of this analytic solution of Equation (4) over the iterative one, lies in the fact that the calculations can be performed with ease, and the feed plate matching accomplished without much difficulty. Also, since the eigenfunctions $v_k(i)$ and the characteristic numbers λ_k are identical with those of the unperturbed model, and are therefore independent of the function $\overset{\circ}{x}_0(i)$, the solution is not very sensitive to the particular form of $\overset{\circ}{x}_0(i)$. It must be kept in mind however, that the perturbation method is only approximate, and, for quantitative results, is reliable only when the perturbations are small.

3. The Extension to Complex Mixtures

The results of the preceding chapter can now be extended to complex mixtures, that is to mixtures with an indefinite number of components. Only continuous mixtures will be considered here, because the generalization of the results to other cases can be carried out without much difficulty.

It was shown in Part I, that, for complex mixtures, the basic equations for an ideal column contain a distribution function in place of the conventional mole fraction; moreover, by definition, the distribution function of a continuous mixture is everywhere continuous, and in addition it will be supposed in this chapter that said distribution function is everywhere positive.

A question arises however concerning the choice of the component designating variable. It will be recalled that in the previous articles the reciprocal relative volatility p was chosen as the component designating symbol. Complications arise however if, as will be supposed here, the reciprocal relative volatility p varies from plate to plate in the cascade. It will be assumed again therefore, that the more simplified model, that is with constant molal overflow and constant relative volatilities, has already been solved, so that fairly reliable estimates exist as to the composition of the mixture and its temperature on each plate. With this information then one could estimate the functional dependence of the relative volatilities and the flows on the plate number.

Throughout this chapter then two independent variables will be used. The one will be the plate designating symbol n and the other will be the "component designating symbol" $\overset{\circ}{p}$, where $\overset{\circ}{p}$ will be the same as the variable p used previously in Part I in connection with the "unperturbed" model. Otherwise the problem to be solved and the method of solution parallel those in the previous section.

The basic equation then, for an ideal enriching column with variable relative volatilities and unequal molal overflow, is

$$y_{n+1}(\overset{\circ}{p}) = \frac{R_n}{R_n+1}\,\frac{p_n(\overset{\circ}{p})\,y_n(\overset{\circ}{p})}{\int_0^\infty p_n(q)\,y_n(q)\,dq} + \frac{\overset{\circ}{x}_0(p)}{R_n+1} \tag{15}$$

The above can now readily be linearized to

$$X_{n+1}(\overset{\circ}{p}) = R_n\,p_{n+1}(\overset{\circ}{p})\,X_n(\overset{\circ}{p}) + p_{n+1}(\overset{\circ}{p})\int_0^\infty x_0(q)\,X_n(q)\,dq \tag{16}$$

where the new dependent variable $X_n(\overset{\circ}{p})$ is defined by

$$p_n(\overset{\circ}{p})\,y_n(\overset{\circ}{p}) = \frac{1}{R_{n-1}+1}\,\frac{x_0(\overset{\circ}{p})X_n(\overset{\circ}{p})}{\int_0^\infty x_0(q)\,X_{n-1}(q)\,dq} \tag{17}$$

Again let

$$p_n(\overset{\circ}{p}) \equiv \overset{\circ}{p} + \overset{\iota}{p}_n(\overset{\circ}{p})$$

$$R_n = \overset{\circ}{R} + \overset{\iota}{R}_n$$

$$x_0(\overset{\circ}{p}) = \overset{\circ}{x}_0(\overset{\circ}{p}) + \overset{\iota}{x}(\overset{\circ}{p})$$

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and $R_0 = \overset{\circ}{R}$ where it is supposed that the perturbations $\overset{1}{p}(\overset{\circ}{p})$, $\overset{1}{R}_n$ and $\overset{1}{x}(\overset{\circ}{p})$ are small in comparison with the unperturbed terms. When the above are substituted in Equation (16) and only the first order perturbation is taken into account, there results that

$$\left.\begin{aligned}\overline{X}_{n+1}(\overset{\circ}{p}) &= \overset{\circ}{R}\,\overset{\circ}{p}\,\overline{X}_n(\overset{\circ}{p}) \\ &+ \overset{\circ}{p}\int_{\overset{\circ}{0}}^{\overset{\circ}{\infty}} \overset{\circ}{x}_0(q)\,\overline{X}_n(q)\,dq \\ &+ \overset{\circ}{R}\,\overset{1}{p}_{n+1}(\overset{\circ}{p})\,\overset{\circ}{X}_n(\overset{\circ}{p}) \\ &+ \overset{1}{R}_n\,\overset{\circ}{p}\,\overset{\circ}{X}_n(\overset{\circ}{p}) \\ &+ \overset{1}{p}_{n+1}(\overset{\circ}{p})\int_{\overset{\circ}{0}}^{\overset{\circ}{\infty}} \overset{\circ}{x}_0(q)\,\overset{\circ}{X}_n(q)\,dq \\ &+ \overset{\circ}{p}\int_{\overset{\circ}{0}}^{\overset{\circ}{\infty}} \overset{1}{x}_0(q)\,\overset{\circ}{X}_n(q)\,dq\end{aligned}\right\} \quad (18)$$

where

$$\overline{X}_{n+1}(\overset{\circ}{p}) \equiv \overset{\circ}{X}_{n+1}(\overset{\circ}{p}) + \overset{1}{X}_{n+1}(\overset{\circ}{p})$$

Finally, Equation 18 can be written as

$$\overline{X}_{n+1}(\overset{\circ}{p}) = \overset{\circ}{H}\,\overline{X}_n(\overset{\circ}{p}) + F_n(\overset{\circ}{p}) + \overset{\circ}{p} f_n \quad (19)$$

where $\overset{\circ}{H}$ is the linear operator for the unperturbed model – see Equation (4·7) of Part I – and

$$f_n \equiv \int_{\overset{\circ}{0}}^{\overset{\circ}{\infty}} \overset{1}{x}_0(q)\,\overset{\circ}{X}_n(q)\,dq \quad (20)$$

Again the function $F_n(\overset{\circ}{p})$ is known, since it contains the solution to the unperturbed problem; and f_n is also known if $\overset{1}{x}_0(\overset{\circ}{p})$ is assumed.

Now to solve Equation (19), use is made of the integral transform introduced in Section 4 of Part I. It will be recalled, that if $f(q)$ is an integrable function of q, then, according to Equation (4·18),

$$T[f(q)] \equiv P\int_{\overset{\circ}{0}}^{\overset{\circ}{\infty}} \frac{f(q)\,\overset{\circ}{x}_0(q)}{\lambda - q}\,dq + \frac{f(\lambda)}{\lambda}\,w(\lambda) \quad (21)$$

where

$$w(\lambda) \equiv \overset{\circ}{R} - P\int_{\overset{\circ}{0}}^{\overset{\circ}{\infty}} \frac{q\,\overset{\circ}{x}_0(q)}{\lambda - q}\,dq \quad (22)$$

If then

$$T[F_n(q)] \equiv \overline{F}_n(\lambda)$$

and

$$T[\overline{X}_n(q)] \equiv C_n(\lambda)\,(\overset{\circ}{R}\lambda)^{n-1}$$

Then it is found from Equations (19) and (4·20), that

$$C_{n+1}(\lambda) = C_n(\lambda) + \frac{\overline{F}_n(\lambda) + \overset{\circ}{R}\,f_n}{(\overset{\circ}{R}\lambda)^n}$$

and therefore

$$C_n(\lambda) = \sum_{j=1}^{n-1} \frac{F_j(\lambda) + \overset{\circ}{R}\,f_j}{\overset{\circ}{R}(\lambda)^j} + C_1(\lambda) \quad (23)$$

where

$$C_1(\lambda) = T\left[\frac{q + \overset{1}{p}_1(q)}{\overset{\circ}{R}}\right]$$

$$= 1 + \frac{1}{\overset{\circ}{R}}\,P\int_{\overset{\circ}{0}}^{\overset{\circ}{\infty}} \frac{\overset{1}{p}_1(q)\,\overset{\circ}{x}_0(q)}{\lambda - q}\,dq + \frac{\overset{1}{p}_1(\lambda)}{\lambda}\,w(\lambda) \quad (24)$$

So, once $C_n(\lambda)$ is calculated, the application of the inversion formulae (4·21) and (4·24) yields that

$$\overline{X}_n(\overset{\circ}{p}) = p\,P\int_{\overset{\circ}{0}}^{\overset{\circ}{\infty}} \frac{C_n(\lambda)\,C(\lambda)\,(\overset{\circ}{R}\lambda)^{n-1}}{\lambda - \overset{\circ}{p}}\,d\lambda$$

$$+ \frac{C_n(\overset{\circ}{p})\,C(\overset{\circ}{p})\,(\overset{\circ}{R}p)^{n-1}}{\overset{\circ}{x}_0(p)}\,w(p) \quad (25)$$

where

$$C(\lambda) = \frac{\lambda\,\overset{\circ}{x}_0(\lambda)}{[w(\lambda)]^2 + [\pi\lambda\,\overset{\circ}{x}_0(\lambda)]^2} \quad (26)$$

Equation (25) then is the approximate solution to Equation (16). Since the function $w(p)$ is known from the solution of the unperturbed problem, the only calculations which have to be performed are connected with the numerical evaluation of the Cauchy principal value of an

improper integral. However, a method for carrying out such calculations has already been presented in Part III.

It can be said, in conclusion therefore, that once the equations for the ideal model, that is the ideal cascade with equal molal overflow and constant relative volatilities, have been solved, then it is possible to extend the results, by the method outlined in this article, to any slightly non-ideal model. The additional computational work needed is shown to be comparatively light. The perturbation method, presented here, can, moreover, readily be applied to the fractionation of any multicomponent and complex mixture.

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Absorption of carbon dioxide by carbonate solutions in a disc column

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Abstract—Results from the study of the various factors which affect the rate of absorption of carbon dioxide by carbonate solutions in a Stephens-Morris disc column are presented. The characteristics of the absorption carried out in the disc column were found to be similar to those of the absorption in packed towers in respect of the following variables : total concentration of the solution, percentage conversion to bicarbonates, rate of liquor flow, and temperature. At 40% conversion to bicarbonate, the absorption coefficients for a solution 1·00 total sodium normality are given by

$$K_G = 1{\cdot}82 \times 10^{-6} (t - 23)\, I^{0{\cdot}47}$$

Absorption coefficients for potassium carbonate solutions are approximately 36% higher than those for sodium carbonate solutions under the same conditions.

Résumé—L'auteur présente les résultats d'une étude sur les différents facteurs qui affectent la vitesse d'absorption du CO_2 par des solutions de carbonate dans une colonne à disques Stephens-Morris. Par rapport à la concentration totale de la solution, au taux de conversion en bicarbonate, à la vitesse d'écoulement de la liqueur et aux températures, les caractéristiques de l'absorption dans cette colonne sont semblables à celles de l'absorption dans des tours à garnissage.

Pour une solution normale en sodium total et avec 40% de conversion en bicarbonate, les coefficients d'absorption sont donnés par :

$$K_G = 1{\cdot}82 \times 10^{-6} (t - 23)\, T^{0{\cdot}47}$$

Pour des solutions de carbonate de potassium les coefficients d'absorption sont dans les mêmes conditions, approximativement 36% plus élevés que pour des solutions de carbonate de sodium.

Introduction

Based on the results for the absorption of carbon dioxide in water, chlorine in ferric chloride solutions, and ammonia in water, the Stephens-Morris disc column has been accepted as having characteristics similar to those of a commercial packed tower for physical absorption [12]. Morris and Jackson [4] have developed a method for the laboratory evaluation of liquid film coefficients for physical absorption in a packed tower based on data obtained on the same system in a disc column. For absorption accompanied by a simultaneous chemical reaction in the liquid phase, there is at present no method available for the prediction of the liquid film coefficients in a full-scale packed tower. The theoretical treatments based on the film theory [5] or the penetration theory [7] are not in accord with experimental results obtained on the disc column [9], and moreover require a knowledge of the kinetics of the liquid phase reaction which is generally unavailable and which is difficult to measure. If it could be shown that the disc column has characteristics similar to those of a packed tower for chemical absorption, it would probably be possible to develop a laboratory method for the evaluation of liquid film coefficients for chemical absorption based on data obtained on the same system in a disc column.

Experimental Apparatus and Procedure

The Stephens-Morris disc column has been described previously [8, 12]. The major dimensions

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of the absorption unit used in this investigation are :

Number of discs	31
Disc diameter (mean)	1·475 cm
Disc thickness (mean)	0·45 cm
Mean perimeter for liquid flow	0·122 ft.
Equivalent diameter for gas flow (dry)	0·052 ft.
Free space (dry)	89%
Absorption surface (dry)	0·184 sq. ft.

The discs are threaded edgeways on a 2-mm glass road and successive discs are maintained at right angles.

Because of the slow rate of absorption of carbon dioxide in the carbonate solutions, the concentrations of the incoming and exit liquor are negligibly different for a column of normal length. The amount of carbon dioxide absorbed cannot be calculated from gas and liquid analyses taken at each end of the column, but may be calculated from the change with time of the concentration in the graduated 2-litre cylinder used as a liquor reservoir. The liquor was pumped from the reservoir to a constant head vessel, and entered the top of the column after passing through a flowmeter (see Fig. 1). Liquid flowed down the discs, was withdrawn at the base through an adjustable lute vessel, and was returned to the reservoir. The liquor in the reservoir was kept well mixed by recirculation through the by-pass at approximately 330 lb. per hr. The inlet liquor temperature was adjusted by means of variable electrical heater in the liquor flow line near the top of the column. A series of runs consisted of taking seven sets of measurements at equal time intervals.

The carbon dioxide was absorbed in sodium carbonate solutions (0·31 to 2·16 normal) or potassium carbonate solutions (0·86 to 1·41 normal) at liquor rates from 34 to 415 lb./(hr.)(ft.) at temperatures from 76°F to 142°F and at percentages converted to bicarbonate from 2 to 87. The amount of carbonate in the liquor was determined by titrating a sample from the reservoir with standard hydrochloric acid solution to phenophthalein, and the total normality by titrating to methyl orange.

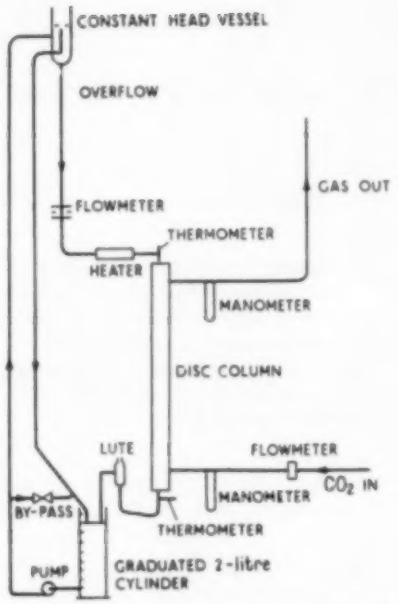

FIG. 1. Outline of the experimental apparatus.

The absorption coefficients are expressed in terms of the gas phase conditions as given by

$$K_G = N_A/A \cdot \Delta p \qquad (1)$$

where N_A is the rate of absorption of carbon dioxide, lb. mol. per hr., A is the surface area of the dry discs, sq. ft. and Δp is the driving force, atm. The amount of carbon dioxide absorbed in one time interval was calculated from the analyses of the liquor in the reservoir at the beginning and end of the time interval and the total volume of liquor in the system, allowance being made for the liquor in the lines and other sections of the apparatus. The total amount absorbed, M, from the beginning of the series is given by the sum of the amounts absorbed in each time interval. The runs, h, were numbered from -8 to $+8$, the central point being O. A fourth-order polynomial was fitted to the experimental relation between M and h by the method of least squares. The constants of the polynomial were evaluated from the solutions derived by AVAKIAN [1]. The slope of the curve, dM/dh, at each integral value of h, was calculated from the constants by the Douglass-Avakian method of numerical differentiation reported by SHERWOOD and REED [11].

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Table 1.

Absorption of carbon dioxide by solutions of sodium carbonate.

Series No.	*Run No. h*	*Time min*	*Total concn. N*	*Γ*	*Temp. °F*	*% bicarb.*	10^3 *M*	*Δp atm*	$\frac{dM}{dh}$	10^3 K_G	K_G *relative to 40 % bicarb.*
1	− 3	0	1·47	341	80	2	0	0·971	0·487	3·63	2·79
	− 2	45		342	80	11	0·414	0·971	0·327	2·44	1·88
	− 1	90		346	81	19	0·696	0·969	0·260	1·95	1·50
	0	135		342	81	22	0·962	0·969	0·230	1·72	1·32
	1	180		343	82	28	1·11	0·964	0·202	1·52	1·17
	2	225		346	83	35	1·31	0·962	0·183	1·38	1·06
	3	270		350	84	40	1·52	0·958	0·172	1·30	1·00
2	− 3	0	0·85	60·3	79	13	0	0·970	0·146	1·09	1·33
	− 2	45		59·9	81	20	0·139	0·965	0·137	1·03	1·26
	− 1	90		59·6	82	26	0·272	0·963	0·127	0·96	1·17
	0	135		59·4	84	33	0·397	0·959	0·118	0·89	1·09
	1	180		59·7	86	39	0·515	0·954	0·109	0·83	1·01
	2	225		60·2	88	44	0·623	0·951	0·098	0·75	0·91
	3	270		60·4	89	48	0·714	0·948	0·089	0·68	0·83
3	− 3	0	0·95	131	85	18	0	0·956	0·190	1·44	1·57
	− 2	45		131	90	25	0·180	0·945	0·161	1·23	1·34
	− 1	90		130	90	32	0·294	0·944	0·139	1·07	1·17
	0	135		131	92	39	0·472	0·940	0·122	0·94	1·02
	1	180		132	91	44	0·581	0·940	0·114	0·88	0·96
	2	225		133	90	50	0·740	0·937	0·107	0·83	0·90
	3	270		132	87	56	0·752	0·938	0·102	0·79	0·86
4	− 3	0	1·38	133	78	15	0	0·951	0·168	1·28	1·46
	− 2	45		132	80	19	0·151	0·949	0·141	1·07	1·22
	− 1	90		131	86	23	0·272	0·945	0·125	0·96	1·09
	0	135		130	87	27	0·394	0·939	0·120	0·93	1·06
	1	180		130	88	30	0·509	0·936	0·118	0·91	1·03
	2	225		130	89	34	0·625	0·934	0·116	0·90	1·02
	3	270		130	90	40	0·740	0·930	0·113	0·88	1·00
5	− 3	0	0·31	33·6	76	39	0	0·956	0·029	0·66	1·02
	− 2	15		33·8	78	45	0·029	0·954	0·027	0·62	0·96
	− 1	30		34·0	79	48	0·055	0·952	0·026	0·60	0·92
	0	45		34·2	79	50	0·083	0·952	0·025	0·57	0·88
	1	60		34·4	80	53	0·105	0·950	0·024	0·54	0·83
	2	75		34·5	81	56	0·129	0·949	0·023	0·52	0·80
	3	90		34·6	81	61	0·151	0·948	0·022	0·50	0·77
6	− 3	0	1·43	395	73	35	0	0·965	0·234	1·76	1·13
	− 2	45		396	76	43	0·202	0·959	0·202	1·52	0·93
	− 1	90		398	78	48	0·394	0·950	0·173	1·32	0·81
	0	135		399	80	55	0·556	0·943	0·157	1·21	0·74
	1	180		400	81	61	0·720	0·932	0·151	1·18	0·73
	2	225		398	82	68	0·883	0·915	0·148	1·17	0·77
	3	270		398	82	73	1·03	0·900	0·145	1·17	0·72

Table 1 (*cont.*)

Absorption of carbon dioxide by solutions of sodium carbonate.

Series No.	*Run No. h*	*Time min*	*Total concn. N*	*Γ*	*Temp. °F.*	*% bicarb.*	$10^3\ M$	*Δp atm*	$\frac{dM}{dh}$	$10^3\ K_G$	*K_G relative to 40 % bicarb.*
7	− 3	0	1·63	136	134	23	0	0·824	0·180	2·38	1·46
	− 2	30		137	132	28	0·162	0·830	0·156	2·05	1·26
	− 1	60		139	133	35	0·312	0·821	0·136	1·79	1·10
	0	90		139	134	40	0·455	0·811	0·121	1·63	1·00
	1	120		138	134	43	0·558	0·810	0·109	1·43	0·88
	2	150		138	135	47	0·663	0·800	0·102	1·38	0·85
	3	180		138	135	51	0·762	0·792	0·100	1·38	0·85
8	− 3	0	1·61	394	127	9	0	0·860	0·428	3·61	1·40
	− 2	45		394	127	18	0·405	0·856	0·390	3·30	1·36
	− 1	90		394	127	28	0·776	0·852	0·347	2·95	1·22
	0	135		374	128	36	1·10	0·842	0·308	2·65	1·09
	1	180		374	129	42	1·39	0·826	0·269	2·36	0·98
	2	225		374	130	51	1·65	0·811	0·234	2·09	0·86
	3	270		374	129	53	1·86	0·802	0·206	1·86	0·77
9	− 3	0	1·43	60·3	114	13	0	0·902	0·207	1·66	1·16
	− 2	45		61·4	116	16	0·198	0·894	0·200	1·62	1·13
	− 1	90		61·4	116	22	0·394	0·892	0·193	1·57	1·10
	0	135		61·4	116	29	0·584	0·889	0·187	1·52	1·06
	1	180		61·4	116	34	0·776	0·885	0·181	1·48	1·03
	2	225		61·4	116	38	0·950	0·882	0·176	1·45	1·01
	3	270		61·4	117	42	1·12	0·874	0·170	1·41	0·99
10	− 3	0	2·14	337	113	15	0	0·895	0·276	2·51	1·17
	− 2	40		338	113	24	0·262	0·898	0·257	2·33	1·09
	− 1	80		338	113	32	0·515	0·896	0·243	2·21	1·03
	0	120		339	113	40	0·752	0·880	0·234	2·15	1·00
	1	160		338	113	47	0·982	0·886	0·227	2·09	0·98
	2	200		337	112	54	1·21	0·876	0·225	2·09	0·98
	3	240		337	113	62	1·43	0·852	0·220	2·10	0·98
11	− 3	0	1·87	189	135	20	0	0·834	0·306	2·39	1·03
	− 2	45		189	135	25	0·301	0·832	0·301	2·36	1·01
	− 1	90		190	135	31	0·602	0·825	0·298	2·36	1·01
	0	135		190	135	36	0·892	0·818	0·293	2·34	1·00
	1	180		190	135	41	1·18	0·810	0·289	2·33	1·00
	2	225		190	134	46	1·47	0·803	0·285	2·32	1·00
	3	270		190	136	51	1·75	0·790	0·279	2·30	0·99
12	− 3	0	1·99	401	136	22	0	0·824	0·479	3·15	1·29
	− 2	60		400	135	30	0·444	0·818	0·420	2·79	1·14
	− 1	120		399	135	38	0·833	0·810	0·373	2·51	1·02
	0	180		398	136	45	1·20	0·790	0·343	2·36	0·97
	1	240		399	135	50	1·54	0·787	0·327	2·26	0·93
	2	300		399	135	54	1·86	0·764	0·318	2·29	0·94
	3	360		400	135	58	2·18	0·732	0·313	2·32	0·96

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Table 1 (*cont.*)

Absorption of carbon dioxide by solutions of sodium carbonate.

Series No.	*Run No. h*	*Time min.*	*Total concn. N*	*Γ*	*Temp. °F.*	*% bicarb.*	10^3 *M*	*Δp atm.*	$\frac{dM}{dh}$	10^3 K_G	K_G *relative to 40 % bicarb.*
13	− 3	0	2·16	48·2	137	25	0	0·806	0·378	2·04	1·51
	− 2	75		48·1	136	34	0·33	0·804	0·293	1·58	1·17
	− 1	150		48·0	136	42	0·59	0·788	0·239	1·32	0·98
	0	225		47·9	137	50	0·81	0·761	0·222	1·27	0·94
	1	300		47·9	137	57	1·06	0·732	0·214	1·27	0·94
	2	375		48·0	137	65	1·26	0·682	0·206	1·31	0·97
	3	450		48·0	137	70	1·37	0·606	0·187	1·34	0·99
14	− 3	0	1·92	372	135	21	0	0·833	0·360	3·52	1·32
	− 2	40		371	135	28	0·336	0·818	0·310	3·09	1·16
	− 1	80		370	135	34	0·602	0·810	0·273	2·75	1·03
	0	120		369	135	43	0·868	0·795	0·258	2·65	1·00
	1	160		369	134	52	1·14	0·776	0·244	2·56	0·96
	2	200		369	135	60	1·38	0·743	0·232	2·55	0·96
	3	240		369	135	64	1·49	0·707	0·225	2·59	0·97
15	− 3	0	2·00	39·0	136	16	0	0·820	0·360	2·39	1·68
	− 2	60		39·4	136	22	0·348	0·815	0·290	1·93	1·36
	− 1	120		39·8	135	27	0·590	0·817	0·252	1·68	1·18
	0	180		41·1	137	31	0·810	0·804	0·230	1·55	1·09
	1	240		40·0	137	35	1·01	0·801	0·218	1·48	1·04
	2	300		39·8	137	40	1·21	0·790	0·209	1·44	1·01
	3	360		39·8	137	45	1·43	0·786	0·202	1·40	0·99
16	− 3	0	1·43	59·6	136	10	0	0·821	0·283	2·50	1·48
	− 2	45		59·4	136	18	0·266	0·820	0·255	2·25	1·33
	− 1	90		59·1	136	26	0·510	0·816	0·230	2·04	1·21
	0	135		58·8	136	33	0·729	0·810	0·209	1·87	1·11
	1	180		58·5	136	39	0·914	0·805	0·189	1·70	1·01
	2	225		58·2	136	45	1·10	0·794	0·175	1·60	0·95
	3	270		58·0	136	51	1·27	0·784	0·168	1·55	0·92
17	− 3	0	1·18	67·9	135	5	0	0·825	0·328	2·88	2·02
	− 2	45		68·8	135	18	0·30	0·822	0·261	2·30	1·62
	− 1	90		69·7	135	28	0·52	0·820	0·208	1·84	1·30
	0	135		70·6	135	37	0·72	0·812	0·172	1·53	1·08
	1	180		70·6	135	43	0·85	0·807	0·146	1·31	0·92
	2	225		70·6	135	50	1·01	0·795	0·126	1·15	0·81
	3	270		70·6	135	55	1·12	0·784	0·108	1·00	0·70
18	− 3	0	1·82	415	134	10	0	0·840	0·534	4·61	1·68
	− 2	45		413	136	20	0·487	0·824	0·429	3·77	1·37
	− 1	90		411	137	30	0·882	0·814	0·360	3·21	1·17
	0	135		408	138	37	1·21	0·804	0·313	2·82	1·03
	1	180		408	135	43	1·52	0·804	0·296	2·67	0·97
	2	225		408	135	50	1·82	0·795	0·284	2·59	0·94
	3	270		408	135	57	2·09	0·761	0·267	2·54	0·92

Table 2. Absorption of carbon dioxide by solutions of potassium carbonate.

Series No.	*Run No. h*	*Time min.*	*Γ*	*Total concn. N*	*% bicarb.*	*Temp. °F.*	$10^3 M$	*Δp atm.*	$\frac{dM}{dh}$	$10^3 K_G$	*K_G relative to 40% bicarb.*
1	− 3	0	397	1·41	9	83	0	0·962	0·389	2·93	1·29
	− 2	45	397		18	83	0·371	0·962	0·362	2·73	1·20
	− 1	90	395		30	81	0·719	0·962	0·320	2·41	1·06
	0	135	393		40	82	1·04	0·959	0·304	2·20	1·01
	1	180	392		51	82	1·33	0·955	0·282	2·14	0·94
	2	225	392		62	82	1·61	0·950	0·276	2·08	0·91
	3	270	392		72	82	1·88	0·937	0·269	2·08	0·91
2	− 3	0	55·1	0·86	2	86	0	0·954	0·260	1·97	1·95
	− 2	45	54·6		12	87	0·232	0·951	0·206	1·57	1·56
	− 1	90	52·8		20	87	0·418	0·951	0·174	1·33	1·32
	0	135	50·9		27	89	0·580	0·948	0·157	1·20	1·19
	1	180	50·6		34	89	0·731	0·948	0·142	1·08	1·07
	2	225	50·3		42	88	0·870	0·948	0·132	1·01	1·00
	3	270	50·0		49	86	1·00	0·950	0·125	0·96	0·95
3	− 3	0	48·8	0·99	4	136	0	0·819	0·255	3·89	1·54
	− 2	30	48·9		14	136	0·244	0·819	0·232	3·08	1·40
	− 1	60	49·0		23	136	0·464	0·817	0·209	2·78	1·26
	0	90	49·1		32	136	0·684	0·815	0·186	2·47	1·12
	1	120	49·4		39	136	0·870	0·813	0·162	2·17	0·99
	2	150	49·7		46	142	1·01	0·779	0·145	2·02	0·92
	3	180	49·9		53	136	1·28	0·805	0·128	1·72	0·78
4	− 3	0	401	0·95	19	136	0	0·817	0·410	5·46	1·40
	− 2	30	401		38	136	0·371	0·815	0·330	4·40	1·13
	− 1	60	401		43	132	0·661	0·829	0·282	3·70	0·95
	0	90	401		53	135	0·940	0·811	0·256	3·43	0·88
	1	120	401		68	131	1·22	0·811	0·234	3·14	0·81
	2	150	401		79	133	1·45	0·775	0·222	3·11	0·80
	3	180	401		87	133	1·62	0·722	0·159	2·39	0·61

The rate of absorption is given by dividing the slope by the length of the time interval in hours. These lengthy calculations were undertaken to eliminate any personal error in measuring the slope form a graph of M against h. The partial pressure of carbon dioxide over the carbonate-bicarbonate solution was determined from equations given by Perry [6, p. 679]. The partial pressure of water vapour of the solution was taken to be the same as that of a sodium carbonate solution of the same total normality, and was determined from data of Perry [6, p. 172]. The partial pressure of carbon dioxide in the gas phase was calculated by subtracting from the total pressure in the column the partial pressure of water vapour. The density of the solution was calculated from data of Perry [6, p. 181].

Results and Discussion

The experimental results for the absorption of carbon dioxide in sodium carbonate solutions are given in Table 1, and for absorption in potassium carbonate solutions in Table 2. The absorption coefficients have been correlated in terms of a standard solution 1·00 total normality 40% converted to bicarbonate.

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Effect of Conversion to Bicarbonate

For each series, the readings were taken at almost constant values of total normality, liquor rate, and temperature. The effect of the conversion to bicarbonate was obtained by plotting the experimental coefficients as a function of the percentage bicarbonate in the solution. The coefficients at 40% bicarbonate was read from the graph, and the relative coefficients were obtained by dividing the experimental coefficients by the figure. The liquor rate, temperature, and driving force, Δp, were plotted on the same graph, and values at

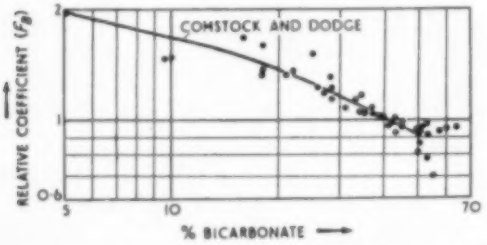

Fig. 2. The effect of the absorption coefficient on the conversion to sodium bicarbonate (one third of the points are plotted).

40% bicarbonate noted. The values of the coefficients, liquor rates, and temperatures read from these graphs are given in Table 3 and are used in the correlations showing the effect of liquor rate, temperature and total normality. The coefficients relative to those at 40% bicarbonate are shown in Fig. 2 for sodium carbonate solutions, and in Fig. 3 for potassium carbonate solutions.

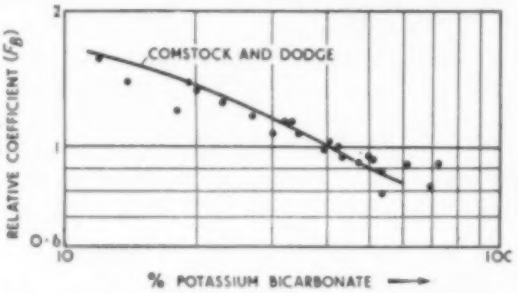

Fig. 3. The effect on the absorption coefficient of the conversion to potassium bicarbonate.

Comstock and Dodge [2] have measured the rates of absorption of carbon dioxide into potassium carbonate solutions over a wide range of conversions to bicarbonate. They used a 3in. diameter tower packed with glass rings 10 mm o.d. × 8 mm i.d. × 10 mm length to a height of 10·67 ft. The relative coefficient corresponding to the arithmetic mean of the per entage bicarbonate in the liquor entering and leaving the tower has been calculated from their data and is shown

Table 3. Absorption of carbon dioxide in carbonate solutions. Data at 40% conversion to bicarbonate.

Series No.	$10^3 K_G$	*Temp. °F.*	Γ	*Total concn. N*	*Series No.*	$10^3 K_G$	*Temp. °F.*	Γ	*Total concn. N*
(a) Data for sodium carbonate solutions									
1	1·30	84	350	1·47	10	2·14	113	339	1·26
2	0·82	87	60·0	0·85	11	2·33	135	190	1·87
3	0·92	92	131	0·95	12	2·45	135	394	1·99
4	0·88	90	130	1·38	13	1·35	136	48·0	2·16
5	0·65	77	33·6	0·31	14	2·66	135	369	1·92
6	1·65	77	395	1·43	15	1·42	137	39·8	2·00
7	1·63	134	139	1·19	16	1·69	136	58·4	1·43
8	2·42	128	374	1·61	17	1·42	135	70·6	1·18
9	1·43	117	61·4	1·49	18	2·75	136	408	1·82
(b) Data for potassium carbonate solutions									
1	2·28	82	393	1·41	3	2·20	136	49·4	0·99
2	1·01	88	50·5	0·86	4	3·90	135	401	0·93

by the lines on Fig. 2 and Fig. 3. These lines represent satisfactorily the data from the disc column.

Effect of Liquor Rate

The correlation between the absorption coefficients and liquor rate, temperature, and total normality was made by the method of successive approximations. The final correlation is

$$K_G = 1{\cdot}82 \times 10^{-6} F_B \cdot F_C (t - 23) \Gamma^{0{\cdot}47} \qquad (2)$$

The effect of liquor rate is shown in Fig. 4. Those series taken at or near 85°F and 135°F were

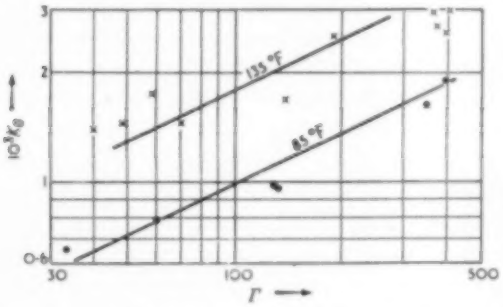

Fig. 4. Correlation of the absorption coefficients with liquor rate for sodium carbonate solutions corrected to 1·00 total normality and 40% conversion to bicarbonate.

corrected for temperature to either 85°F or 135°F and for concentration to 1·00 total normality. The equations for the lines on Fig. 4 are

$$K_G = 0{\cdot}113 \times 10^{-3} \Gamma^{0{\cdot}47} \qquad (3)$$

at 85°F, and

$$K_G = 0{\cdot}204 \times 10^{-3} \Gamma^{0{\cdot}47} \qquad (4)$$

at 135°F. A different slope at the two temperatures would fit the data better, but the difference between the slopes is small considering the scatter of the data.

Furnas and Bellinger [3] have studied the rates of absorption of carbon dioxide in sodium carbonate solutions, using a 12in. diameter tower packed with ⅜ in. and 1 in. Raschig rings and 1 in. Berl saddles. For physical absorption, the liquid film coefficients are proportional to the 0·54 power of the liquor rate for ⅜ in. rings, to the 0·76 power for 1 in. rings, to the 0·65 power for 1 in. saddles [10], and to the 0·7 power for discs [8, 12]. It is possible that the liquid film coefficients in a packed tower can be related to those in a disc column by

$$k_L a \propto L^{nx} \qquad (5)$$

where n is the slope of the coefficient-liquor rate line plotted on log-log paper for the absorption when carried out in the disc column, and x is the ratio of the slope for physical absorption in a

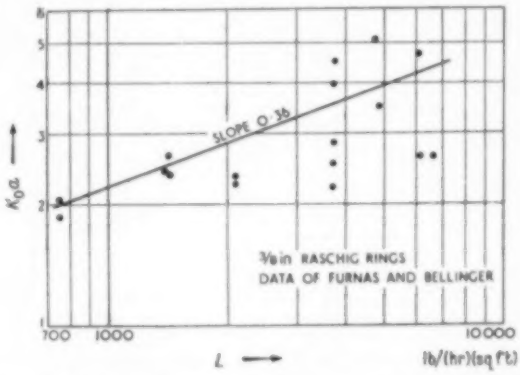

Fig. 5. Data of Furnas and Bellinger for ⅜ in. Raschig rings compared to the predicted slope.

packed tower to the slope for physical absorption in a disc column. On this basis, x is 0·54/0·7, or 0·77, for ⅜ in. rings, 1·09 for 1 in. rings, and 0·93 for 1 in. saddles. The corresponding slope for the absorption of carbon dioxide in sodium carbonate solutions are 0·47 × 0·77, or 0·36, for ⅜ in. rings, 0·51 for 1 in. rings, and 0·44 for 1 in.

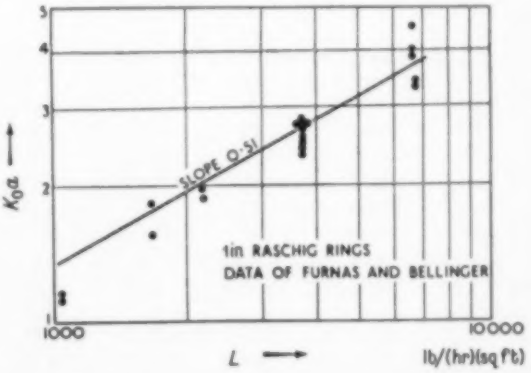

Fig. 6. Data of Furnas and Bellinger for 1 in. Raschig rings compared to the predicted slope.

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saddles. The data of FURNAS and BELLINGER has been recalculated and corrected to 85°F, 1·00 total normality, and 40% conversion to bicarbonate using equation (2). The data for $\frac{3}{8}$ in. rings are shown in Fig. 5, for 1 in. rings in Fig. 6, and for 1 in. saddles in Fig. 7. The data in Fig. 5 scatter badly and no conclusion can be drawn, but the data of the other two figures show that the predicted slope is in good agreement with the experimentally determined slopes.

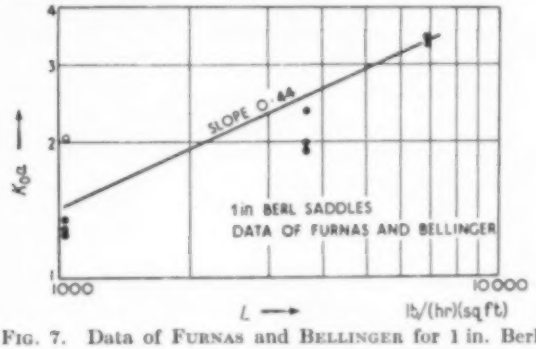

FIG. 7. Data of FURNAS and BELLINGER for 1 in. Berl saddles compared to the predicted slope.

The data of COMSTOCK and DODGE [2] using glass rings cannot be correlated in this manner due to the unknown effect on the liquid film coefficient for physical absorption of the small diameter of their column, and of the large height of packing without redistribution of the liquor. Their data have been recalculated to 1·00 total normality and 40% conversion to potassium bicarbonate at temperatures of 59°F, 104°F and 133°F, and is plotted in Fig. 8. Part only of their 28 runs at temperatures near 59°F is shown, but all the runs near 104°F and 133°F are shown. Within the accuracy of the data and the same slope is applicable at each of the temperatures.

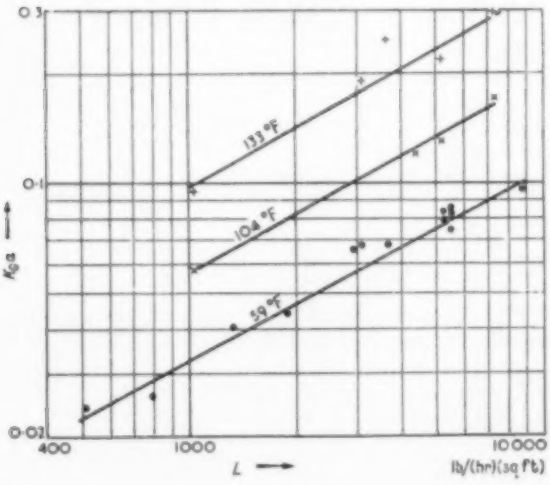

FIG. 8. Data of COMSTOCK and DODGE showing the effect of liquor rate at various temperatures on the absorption coefficient using potassium carbonate solutions.

EFFECT OF TEMPERATURE

The experimental coefficients were corrected for liquor rate, total normal normality and conversion to bicarbonate. The coefficient at 85°F was taken as unity, and the coefficients relative to 85°F calculated. The data are shown in Fig. 10. The points at 85°F and 135°F are taken from the lines of Fig. 5, and therefore represent a large number of individual coefficients. The points from the data of COMSTOCK and DODGE [2] were taken from the lines of Fig. 9, and represent a large number of individual coefficients. The data of Fig. 9 can be correlated by one line, showing that the effect of temperature on the absorption in a disc column is in close agreement with the effect of temperature in a packed tower.

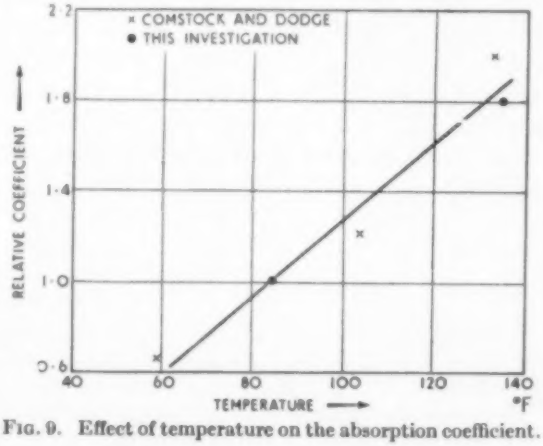

FIG. 9. Effect of temperature on the absorption coefficient.

EFFECT OF TOTAL CONCENTRATION

The effect of total concentration is small, almost within experimental error. COMSTOCK and DODGE [2] have found that an increase in total concentration decreases the coefficient slightly. The data of this investigation were divided into

sections of low, medium and high concentrations. The coefficients corrected for temperature, liquor rate, and conversion to bicarbonate, were averaged in each section. These data are shown in Fig. 10. The line representing the results of COMSTOCK and DODGE is shown on the same figure. Within experimental error, the effect of total concentration is the same for both columns.

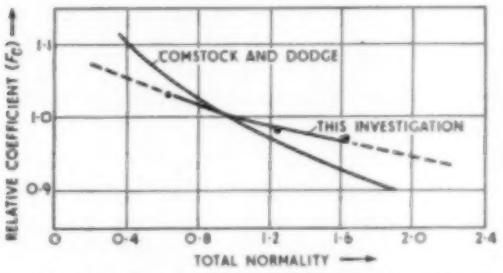

FIG. 10. Effect of total normality on the absorption coefficients.

COMPARISON OF SOLUTIONS OF SODIUM AND POTASSIUM CARBONATES

In addition to their extensive data for potassium carbonate solutions, COMSTOCK and DODGE give data obtained using sodium carbonate solutions. Compared under similar conditions of temperature, total concentration and conversion to bicarbonate, their coefficients for potassium carbonate solutions are approximately 40% higher than their coefficients for sodium carbonate solutions. The coefficients for the disc column given in Table 3 show that those coefficients for potassium carbonate solutions are 36% higher than the coefficients for sodium carbonate solutions.

CONCLUSION

The disc column has been compared to packed towers for the absorption of carbon dioxide by carbonate solutions. The disc column shows characteristics similar to those of packed towers for the absorption in respect to the effect on the absorption coefficient of the liquor rate, the total normality of the solution, the percentage conversion to bicarbonate and temperature.

Acknowledgements—The author wishes to acknowledge the continued interest of Professor J. P. BAXTER in this work.

NOTATION

a = surface area of dry packing, sq. ft. per cu. ft.
A = surface area of dry discs, sq. ft.
F_B = factor to allow for the conversion to bicarbonate (i.e. the coefficient relative to the coefficient at 40% bicarbonate)
F_C = factor to allow for the effect of total normality (i.e. the coefficient relative to the coefficient at 1·00 total normality)
h = the number of a run in a series, taken at equal time intervals
k_L = the liquid film coefficient of absorption, ft. per hr.
K_G = the overall coefficient of absorption based on gas film conditions, lb. mol./(hr.) (sq. ft.) (atm.)
K_0 = the overall coefficient of absorption based on gas film conditions, lb./(hr.) (sq. ft.) (atm.)
L = rate of liquor flow in a packed tower, lb./(hr.) (sq. ft.)
M = the amount of carbon dioxide absorbed, lb. mol.
N = total normality
N_A = the rate of absorption of carbon dioxide, lb. mol. per hour
Δp = the driving force for absorption, atm.
t = temperature, °F.
Γ = rate of flow of the liquor, lb./(hr.) (ft.)

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The effect of a surface-active agent on mass transfer in a stirred liquid-liquid extractor*

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Abstract—The effect has been observed of small additions of sodium oleyl-*p*-anisidinesulphonate on the rate of extraction of iodine from aqueous solutions with carbon tetrachloride in an agitated extractor. The results have been analysed by the method of Hixon and Smith [2]. The time required for extracting 90% of the extractable iodine from the aqueous phase increased with the concentration of surface-active agent to a maximum about 70% above the original value at 3×10^{-5} g/100 ml aqueous solution, and fell on further additions far below the original value. The Hixon lines were curved for the larger additions of surface active agent, indicating a gradual increase in interfacial area.

Résumé—Les auteurs ont étudié l'effet produit par l'addition de petites quantités de sulfonate de sodium d'oleyl-*p*-anisidine, sur la vitesse d'extraction de l'iode à partir de solutions aqueuses au moyen de $C Cl_4$, dans un extracteur agité. Les résultats ont été analysés par la méthode de Hixon et Smith. Le temps nécessaire à l'extraction de 90% de l'iode que peut fournir la phase aqueuse, croit avec la concentration de l'agent tensio-actif jusqu'à un maximum de 70% environ de la valeur primitive de 3×10^{-5} g pour 100 moles de solution aqueuse. Les courbes de Hixon s'infléchissent pour des additions plus importantes d'agent tensio-actif, ce qui indique une augmentation graduelle de la surface à l'interface.

Introduction

In recent years several investigators have studied the effect of surface-active agents on the rate of mass transfer in liquid-liquid extraction. Both spray and packed columns have been used, as well as agitated systems. The most important papers on the subject have been reviewed recently by Garner and Hale [3] who have themselves found that the rate of extraction of diethylamine from toluene by drops of water was reduced to 45% of the original value by the addition of 0·015% *Teepol*. They were able to show that this retardation appeared also with droplets which did not exhibit internal circulation. Although the literature is not unanimous, a considerable amount of evidence has been accumulated to show that surface-active agents, adsorbed at an interface between two liquids, can effect a substantial reduction in the rate of mass transfer. There is, however, still insufficient data available to enable firmly based conclusions to be drawn with regard to the nature of this effect.

The present work was carried out as a preliminary to further investigations. A stirred tank extractor was used, and the results were analysed by the method of Hixon and Smith [2]. The system studied by these authors, viz. carbon tetrachloride – water – iodine, was chosen also for the present work, and sodium oleyl–*p*–anisidinesulphonate was selected as surface-active agent.

Experimental

The apparatus was in principle similar to that used by Hixon and Smith [2], and is illustrated in Fig. 1.

A cylindrical glass vessel of about 4 litre total capacity was equipped with a simple paddle stirrer driven at 140 ± 1 r.p.m., and arranged with its lower edge at the interface as shown. The vessel was placed in a water bath which was thermostatically controlled at 22·0°C. In all experiments the volume of the aqueous phase was 10 times that of the organic phase.

* A summary of this paper has appeared elsewhere [1].

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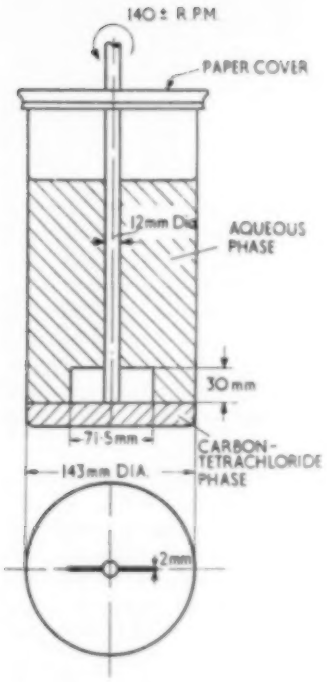

FIG. 1. Extraction apparatus.

Iodine of standard analytical quality was dissolved in distilled water to give a concentration of about 230 mg/l. 8 litres of this solution was added to the apparatus, which was covered with paper to reduce loss of iodine by evaporation. The stirrer was started, and a sample taken. 800 ml of refractionated, commercial carbon tetrachloride was added carefully through a funnel which reached nearly to the bottom of the vessel. The extraction process was followed by photometric determinations of iodine in samples withdrawn from the vessel. During the runs only the aqueous phase was sampled, but at the end the organic phase was also analysed as a cheque on the material balance. The volume of the samples withdrawn was compensated for as described by HIXON and SMITH.

With no addition of surface-active agent the action of the agitator caused wave-formation at the interface, but very few droplets of carbon tetrachloride were detached from the main bulk. With increasing additions, more free droplets were observed, and with still larger additions a froth appeared at the interface. In no case was more than a small fraction of the organic phase dispersed.

The surface-active agent was obtained as *Lissapol LS*, a commercial product of the *I.C.I. Ltd.*, Dyestuffs Division. This was dissolved in warm *n*-butanol, filtered, crystallized several times, and finally washed with ether and dried. For the present experiments a stock solution was made containing per 100 ml :

0·1023 g sodium oleyl-*p*-anisidinesulphonate
0·1656 g sodium sulphate
0·0225 g sodium chloride

Stock solutions older than 14 days were discarded. In the present paper all concentrations of surface-active agent are expressed as g of the active component per 100 ml of the aqueous phase.

RESULTS

On the basis of the two-film theory of extraction, HIXON and SMITH [2] have deduced that a plot of $\log\left(1 - \frac{W_E}{W_{E\,eq}}\right)$ against time should give a straight line, provided the interfacial area and the partition coefficient remain constant throughout a run. The value of PEARCE and EVERSOLE [4] for the partition coefficient at 25°C,

$$m = 83{\cdot}7\,\frac{\text{mg iodine per ml carbon tetrachloride}}{\text{mg iodine per ml water}}$$

has been used in the present work. This gives $W_{E\,eq} = 0{\cdot}893 \times W^{\circ}_{B}$ which enables the HIXON curves to be plotted. The results of some typical runs are shown in Fig. 2.

It can be seen that the lines are straight except for the larger additions of surface-active agent. The deviation from the straight line indicates an increase of the interfacial area with time, and makes it impossible to characterize a run by a single constant as HIXON and SMITH have done. Instead, the time t_{90} required for extracting 90% of the extractable iodine ($W_E = 0{\cdot}9 \times W_{E\,eq}$) was noted as well as $2 \times t_{68\cdot4}$, where $t_{68\cdot4}$ is the time required to give $W_E = 0{\cdot}684 \times W_{E\,eq}$. For a straight line these figures should be the same, and the difference can be taken to give a measure of the departure from linearity.

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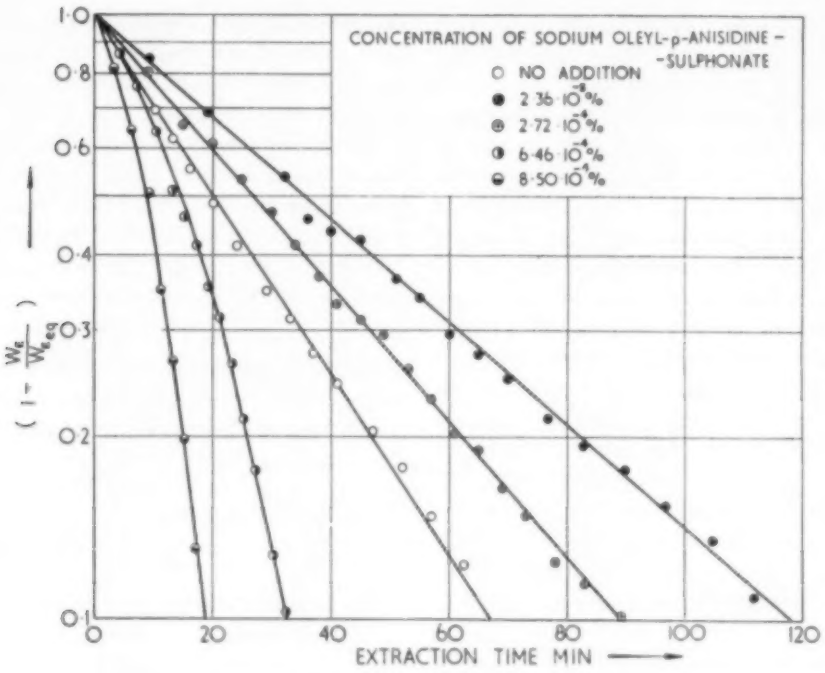

FIG. 2. Typical runs with and without surface active agent, plotted according to HIXON and SMITH [2].

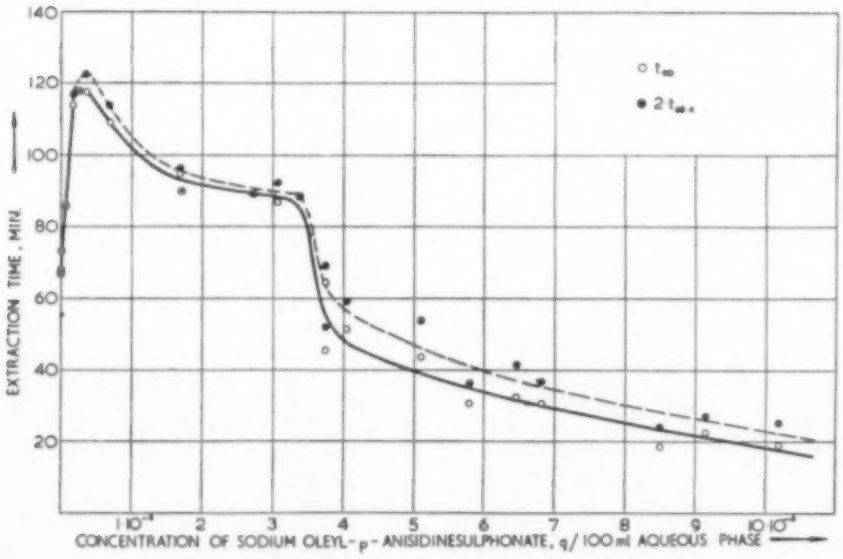

FIG. 3. Time for extracting 90% of extractable iodine, t_{90} and $2 \times t_{68\cdot4}$ plotted against concentration of surface active agent.

The results have been summarized in Fig. 3, where t_{90} and $2 \times t_{68\cdot4}$ are plotted against the concentration of surface-active agent.

With increasing concentration, the extraction times increase to a value about 70% above the original at 3×10^{-5} g/100 ml, and subsequently fall well below the original. These results are analogous to those obtained by CHU, TAYLOR and LEVI [5] from measurements of the rate of extraction of benzoic acid from benzene into water in a packed column. At small concentrations of weak surface-active agents there is a retardation of the mass transfer due to the molecules adsorbed at the interface, but at higher concentrations the tendency of the agent to increase the interfacial area predominates. At about $3{\cdot}7 \times 10^{-4}$ g/100 ml a sudden decrease in the extraction time resulted from a small addition of surface, active agent. This critical concentration was found to vary greatly with the speed of the agitator.

These results differ from those already reported in the literature by the extremely small concentrations of surface-active agent found to be effective in reducing the rate of mass transfer, 1 part per 10^7 parts of water being sufficient to give a noticeable effect. The effective concentration is thus about 500 times smaller than that reported for *Teepol* by GARNER and HALE [3]. It can be seen from Fig. 3 that t_{90} and $2 \times t_{68\cdot4}$ are equal for concentrations of surface active agent less than about 2×10^{-5} g/100 ml, which means that the theory of HIXON and SMITH holds in this range. This result indicates that the process responsible for the retardation of mass transfer is established more rapidly than the extension of the interfacial area caused by the larger concentrations of surface-active agent.

Acknowledgement—The authors wish to thank the Royal Norwegian Research Council for a grant which enabled this work to be carried out.

NOTATION

m = Partition coefficient : $\dfrac{\text{mg iodine per ml of solvent phase}}{\text{mg iodine per ml of aqueous phase}}$

W_E = Weight of solute in extract phase (organic) g

$W_{E\,eq}$ = Weight of solute in extract phase (organic) after equilibrium is established g

W_R° = Weight of solute in raffinate phase (aqueous) at the start of the experiment g

t_{90} = Time required for extracting 90% of the extractable iodine ($W_E = 0{\cdot}9 \times W_{E\,eq}$) min

$t_{68\cdot4}$ = Time required to give $W_E = 0{\cdot}684\, W_{E\,e}$ min

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A simple method of measuring gaseous diffusion coefficients

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Abstract—In this paper a new and simple method of measuring gaseous diffusion coefficients is described. The method was developed so as to enable coefficients to be readily obtained with sufficient accuracy for design purposes. The method consists essentially in measuring the amount of equi-molar counter-diffusion occurring in a known time along a tube of known bore and length connecting two reservoirs initially containing gas mixtures of different concentrations.

Values of diffusion coefficients obtained by this method are compared with previous measurements for two of the gases, and satisfactory agreement is found. Coefficients are given for the diffusion of CO_2, NH_3, SO_2, Cl_2 and Br_2 in air at 20°C and 760 mm Hg pressure.

Résumé—L'auteur décrit une méthode simple et nouvelle pour mesurer rapidement et avec une précision suffisante, les coefficients de diffusion gazeuse. La méthode comporte essentiellement la mesure de la diffusion à contre-courant d'un nombre égal de molécules, dans un tube (section et longueur connues) nécessitant deux réservoirs contenant au départ, des mélanges gazeux de concentrations différentes. L'auteur trouve ses résultats en accord avec ceux des auteurs précédents. Il donne les coefficients pour la diffusion de CO_2, NH_3, SO_2, Cl_2 et Br_2 dans l'air à 20° et sous 760 mm.

Apparatus and Procedure

A knowledge of the gaseous diffusion coefficient for a specified gas mixture is frequently necessary for the design of absorption and stripping towers. Reference to published tables of physical properties too often shows the desired diffusion coefficient to be missing. The method of measurement to be described was developed so as to enable gaseous diffusion coefficients to be readily obtained with sufficient accuracy for design purposes.

The apparatus used, sketched in Fig. 1, is of very simple construction, consisting of two flasks of about 2 litres capacity connected by a glass tube of about 0·7 cm bore and 24 cm long having a stopcock of the same bore in the centre. The flasks are set up with connecting tube vertical in a large (150 litres) unheated water bath. Other connections to the flasks, shown in the sketch, permit filling and purging either flasks and also connection of the flasks to an absorber vessel. The latter consists of a horizontal tube partially filled with an absorbent liquor or granulated absorbent depending on the gaseous diffusion coefficient being measured.

When using this apparatus for measuring the diffusion coefficient of, for instance, a certain gas in air, one of the flasks is initially filled with a mixture of air and the gas, the stopcock in the diffusion tube being closed as also are the connections to the absorber. The other flask is filled with air to approximately the same pressure. If the gas is lighter than air, the mixture is introduced into the upper flask, if heavier the lower flask is filled with the gas mixture. The density difference thus opposes convective transfer between the flasks when the stopcock in the diffusion tube is opened.

After filling, the whole apparatus shown in the sketch is left in the water bath for several hours, rapid stirring ensuring the attainment of a constant temperature throughout the mass. In order to eliminate any bulk flow through the diffusion tube which would occur when the stopcock is opened if the gas pressures in the two flasks were unequal, both flasks are connected to the absorber for a period prior to opening the stopcock in the diffusion tube. The absorber acts as a trap for the gas contained in the air/gas mixture and ensures that only air can be

transferred from one flask to the other during the final pressure equalising operation. Both flasks are then isolated from the absorber and the stopcock in the diffusion tube is opened. Equimolar counter diffusion of the gas and air along the diffusion tube is then allowed to proceed for from one to five days, after which the stopcock is closed and the contents of each flask are analysed.

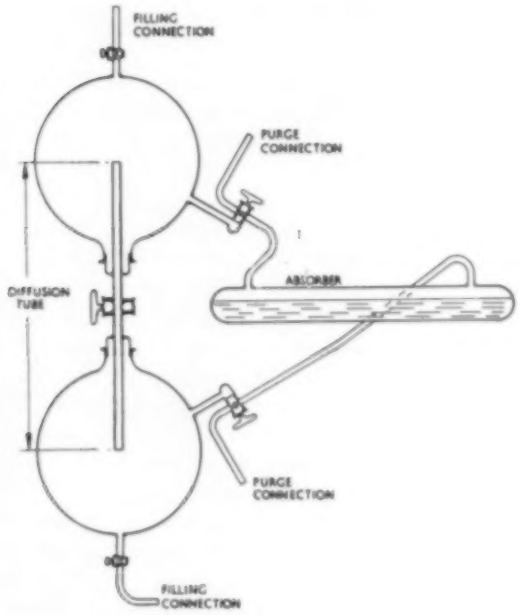

Fig. 1. Sketch of diffusion apparatus.

INTERPRETATION OF RESULTS

The process taking place while the stopcock is open is essentially that of equi-molar counter diffusion of the two gas species along a tube of known length and cross-section resulting from the concentration difference between the two ends of the tube.

Thus if l = Effective length of diffusion tube = true length + end corrections.

a = Cross-sectional area of diffusion tube.

Q = Quantity of either species transferred in time (t), expressed as the volume of pure gas at the total pressure and temperature in the apparatus.

D = Diffusion coefficient under prevailing conditions of temperature ($T°$ K) and pressure (p) in the apparatus.

ΔC_0 = Initial concentration difference of one species between the two flasks, concentration being expressed on a volumetric ratio basis.

ΔC_t = Concentration difference at time (t) of this species between the two flasks.

Then ignoring the transfer associated with setting up the initial linear concentration gradient along the tube, at any instant :—

$$\frac{dQ}{dt} = \frac{Da}{l}\,\Delta C_t \qquad (1)$$

Now if v_1 and v_2 are the volumetric capacities of the two flasks then :—

$$\frac{-\,d\,(\Delta C_t)}{dt} = \left(\frac{1}{v_1} + \frac{1}{v_2}\right)\frac{dQ}{dt} \qquad (2)$$

Substituting for $\frac{dQ}{dt}$ from (1) in (2) gives :—

$$\frac{-\,d\,(\Delta C_t)}{\Delta C_t} = \frac{Da}{l}\left(\frac{1}{v_1} + \frac{1}{v_2}\right)dt$$

Integrating from $\Delta C_t = \Delta C_0$ to $\Delta C_t = \Delta C_t$ and $t = 0$ to $t = t$ then :—

$$D = \frac{l}{at}\left(\frac{1}{\frac{1}{v_1} + \frac{1}{v_2}}\right)\ln\frac{\Delta C_0}{\Delta C_t}$$

or as $\quad Q\left(\frac{1}{v_1} + \frac{1}{v_2}\right) = \Delta C_0 - \Delta C_t$

then :— $\qquad D = \dfrac{lQ\ln\left(\frac{\Delta C_0}{\Delta C_t}\right)}{at\,(\Delta C_0 - \Delta C_t)}$

The length (l) is the effective length of the diffusion tube and comprises the true length plus two end corrections which allow for the

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resistance to transfer associated with spreading of the diffusing species from the ends of the tube throughout the volume of the flasks. Each end resistance is virtually equivalent to the resistance to transfer from one side of a circular flat disc into a surrounding infinite medium. This case has been solved mathematically [1], the resistance being equivalent to a uniform layer of fluid on the disc having a thickness of $\pi d/8$ where d is the disc diameter. Hence :—

$$l = \text{True length of diffusion tube} + \pi d/4.$$

For the apparatus used, the end correction amounted to about 2% of the effective length of the diffusion tube.

In deriving the above expression for calculating the diffusion coefficient, the unsteady state transfer necessary to set up the initial linear concentration gradient which follows the discontinuous gradient existing before opening the stopcock, has been ignored. The unsteady state transfer associated with the changing concentration profile in the tube during the run has similarly been ignored. The volume of gas contained in the diffusion tube is relatively quite small compared with the total transfer during a run, and with runs of over one day's duration it can be shown that the maximum error resulting from neglecting the unsteady state effects is less than ½% in the value of the diffusion coefficient.

Some Coefficients Measured

In order to effect a comparison between the values of diffusion coefficients obtained using the simple apparatus and those measured previously by other investigators using more conventional methods, a series of measurements was made of the diffusion coefficient of dilute CO_2 in air at about normal temperature and pressure. The results of six independent measurements with the simple apparatus are given in Table I, the values of the diffusion coefficient being reduced to 20°C and 760 mm Hg pressure by assuming that the coefficient is inversely proportional to the pressure and proportional to the 7/4 power of the absolute temperature.

The principal dimensions of the diffusion tube and flasks employed for the above measurements are :—

True length of diffusion tube	23·4 cm
Mean cross section of diffusion tube	0·410 cm²
Volumetric capacity of upper flask	2300 cm³
Volumetric capacity of lower flask	2278 cm³

The above six runs give a mean value of 0·165 cm²/sec. with a mean deviation of 0·003 cm²/sec. Recent work by Boyd *et al*, [2]. using a conventional double cell apparatus, but employing an interferometer for following the unsteady state diffusion, gave a value of 0·160 cm²/sec. for the diffusion coefficient of dilute CO^2 in N_2 at 20°C and 760 mm Hg. Previously Boardman

Table I. Measurements of Diffusion Coefficient of Dilute CO_2-Air.

t	hours	39·66	63·75	64·67	66·0	66·5	111·5
p	mm Hg	755	760	755	765	745	765
T	°K	293	293	293	291	292	291
ΔC_0	—	0·1132	0·1108	0·1121	0·1136	0·1074	0·1035
ΔC_t	—	0·0788	0·0632	0·0646	0·0638	0·0589	0·0384
Q	cm³	39·4	54·5	54·4	56·9	55·5	74·5
D	cm²/sec.	0·170	0·164	0·164	0·159	0·170	0·167

and WILD (1937) using a double cell apparatus obtained a value of 0·163 cm^2/sec. for the same system.

A series of twelve measurements using runs of from 16 to 70 hours duration have also been made to determine the diffusion coefficient of dilute NH_3 in air. These gave a mean value for the coefficient at 20°C and 760 mm Hg of 0·227 cm_2/sec. with a mean deviation of 0·008 cm_2/sec. This may be compared with 0·225 cm_2/sec. obtained by WINTERGEIST [4].

Other coefficients measured with the apparatus are :—

Dilute SO_2 – Air $D_{20}° = 0·122$ cm^2/sec. ; mean deviation 0·005 cm^2/sec.

Dilute Br_2 – Air $D_{20}° = 0·091$ cm^2/sec. ; mean deviation 0·004 cm^2/sec.

Dilute Cl_2 – Air $D_{20}° = 0·124$ cm^2/sec. ; mean deviation 0·002 cm^2/sec.

No previous measurements of these three coefficients have been traced.

It appears from the above figures that this type of apparatus can be used for obtaining reproducible values for gaseous diffusion coefficients. Values are in satisfactory agreement with those measured by other means where this has been done.

NOMENCLATURE

a	= Cross-sectional area of diffusion tube.	cm^2
D	= Gaseous diffusion coefficient	cm^2/sec.
l	= Effective length of diffusion tube	cm
p	= Total gas pressure in apparatus	mm Hg.
Q	= Volume (at pressure p and temperature T) of either species transferred during run	cm^3
t	= Duration of diffusion run	sec.
T	= Gas temperature in apparatus	°K
ΔC_0	= Initial concentration difference of one species between the two flasks	—
ΔC_t	= Concentration difference at end of run of one species between the two flasks	—

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Extraction of acetic acid from water

4. Ternary-vapour-liquid equilibrium data

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Abstract—This paper presents ternary vapour-liquid equilibrium data for the system ethyl acetate-acetic acid-water. The data correlates satisfactorily, and linear interpolation can be used to predict the ternary vapour liquid equilibria from the binary data when an appropriate correction factor is used.

Résumé—Les auteurs presentent des résultats relatifs à l'équilibre liquide-vapeur du système ternaire acétate d'éthyle-acide acétique-eau.

La corrélation des données est satisfaisante et il est possible, en tenant compte d'un facteur de correction convenable, de prévoir par une interpolation linéaire, l'équilibre ternaire à partir des données binaires.

Introduction

The system ethyl acetate-acetic acid-water is of great commercial interest but there has been little information published on ternary vapour liquid equilibria; accurate data on this subject are required both in the analysis of the operating conditions of azeotropic columns and for the design of plants of higher efficiencies.

Experimental

The reagents used in the determinations were of the same purity as those described in previous papers, Part 1, 2 and 3.

When both the vapour condensate and the liquid phase in equilibrium were single phase, the equilibrium still of Ellis [24] was used. When the liquid and condensate phases were partially immiscible, the still described by Selvaratnam [34] was used.

A binary mixture of acetic acid and water was made up and was diluted with ethyl acetate after each determination.

Experimental results were thus determined along a line of constant molal ratio of acetic acid to water. After allowing three hours for equilibrium to be established, the liquid and vapour condensate were sampled into ice-cooled bottles. When a single phase was present, samples were then analysed immediately for water and acetic acid content by titration with Fischer reagent and barium hydroxide respectively. When ethyl acetate was present in small quantities the ethyl acetate was estimated by saponification with potassium hydroxide solution.

If either the vapour or liquid condensate was two phase, a known weight of alcohol was added to produce miscibility. This method was preferable to separating the two liquid phases and analysing them separately, as the samples were small and often difficult to separate.

Results

The vapour-liquid equilibrium data are listed in Table 14 and are represented in Figs. 14 to 19. The activity coefficients were calculated according to the equation :

$$\gamma_1 = \frac{\pi y_1}{P_1 x_1} \qquad (1)$$

where γ_1 = activity coefficient of component 1

π = total pressure

y_1 = mole fraction of component 1 in the vapour

x_1 = mole fraction of component 1 in the liquid

P_1 = vapour pressure of component 1 at the temperature of the determination.

Table 14. *Ternary data. Water-acetic acid-ethyl acetate.*

Temp. °C	Press. (mm)	x_w	x_a	x_e	y_w	y_a	y_e	P_a	P_w	P_e	γ_a	γ_w	γ_e	Liquid			Vapour		
														$\frac{W}{A+W}$	$\frac{E}{E+W}$	$\frac{A}{A+E}$	$\frac{W}{A+W}$	$\frac{E}{E+W}$	$\frac{A}{A+E}$
93·8	742·5	45·3	46·4	8·3	48·2	21·4	30·4	327·5	604·1	1275	1·015	1·31	2·14	49·4	15·45	84·75	69·25	38·6	41·3
98·5	751	8·16	72·0	19·8	14·7	40·5	44·8	400	720·1	1455	1·055	1·87	1·162	10·17	71·0	78·5	26·5	75·5	47·5
95·0	755	7·24	64·0	28·8	13·1	30·4	56·5	352·5	633·9	1320	2·16	2·16	1·125	10·15	80·0	69·0	30·2	81·1	35·0
93·1	745	6·5	61·5	32·0	12·0	27·4	60·6	332·5	590·8	1250	0·998	2·32	1·13	9·56	83·2	65·8	30·4	83·5	31·1
90·1	736	5·5	55·0	39·5	10·0	21·9	68·1	295	527·8	1140	0·991	2·55	1·11	9·08	87·8	58·3	31·5	87·2	24·3
88·9	735	4·77	51·5	43·7	9·0	19·0	72·0	282·5	504·2	1100	0·96	2·76	1·10	8·48	90·25	54·0	32·2	88·9	20·9
87·0	738	4·1	45·0	50·9	7·9	15·1	77·0	265	468·7	1040	0·25	3·04	1·076	8·35	92·5	47·0	34·4	90·75	16·35
85·9	759	3·46	39·6	56·9	6·92	11·4	81·7	254	449·2	1008	0·86	3·38	1·08	8·03	94·25	41·0	37·8	92·1	12·22
83·7	752·5	2·6	32·7	64·7	5·41	8·25	86·3	235	412	940	0·808	3·8	1·067	7·36	96·14	83·6	39·6	94·1	8·71
82·2	752·5	2·29	26·5	71·2	4·67	6·31	89·0	222	388·1	900	0·806	3·95	1·045	7·95	96·88	27·2	42·5	95·0	6·62
81·5	755	1·63	22·6	75·8	3·93	4·71	91·4	215	377·3	880	0·733	4·825	1·034	6·73	97·9	23·0	45·5	95·8	4·9
80·7	754	1·4	19·3	79·3	3·72	3·61	92·7	209	363·5	855	0·674	5·49	1·03	6·77	98·3	19·6	50·8	96·1	3·8
79·1	730	1·16	16·2	82·6	3·22	3·22	93·6	196	342·4	815	0·741	5·9	1·01	6·72	96·8	16·4	50·0	96·7	3·3
106·3	757·5	15·2	80·0	4·85	25·6	25·6	58·8	520	960	1790	1·051	1·33	1·36	16·0	24·6	94·27	30·8	38·4	78·5
100·1	957·5	13·4	72·2	14·4	21·0	44·8	34·2	418	762·7	1520	1·125	1·56	1·18	15·56	51·8	83·4	32·0	62·0	56·8
93·5	757	19·19	59·9	20·2	27·0	26·3	46·7	333	600	1260	0·99	1·71	1·375	24·9	50·5	74·8	50·8	63·4	36·0
91·1	750·5	17·1	56·3	26·6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
89·4	753	14·9	53·3	31·8	21·0	21·2	57·8	288	514	1120	1·035	2·06	1·215	21·8	68·1	62·5	49·8	73·4	26·8
101·3	759	35·0	60·8	4·17	45·0	38·0	16·9	437·5	796	1575	1·082	1·222	1·95	36·6	10·65	93·9	54·1	27·3	69·0
94·8	754	33·3	55·3	11·4	39·0	27·6	33·4	350	629·3	1310	1·075	1·4	1·67	37·7	25·6	82·9	58·5	46·1	45·3
90·75	753·5	29·0	51·6	19·4	33·5	20·6	45·9	302	541	1160	1·995	1·6	1·53	36·0	40·1	72·8	63·0	57·8	31·0
88·3	755	25·8	48·5	25·7	30·3	16·3	53·4	277	490	1085	0·915	1·81	1·455	34·6	50·0	64·5	65·0	63·8	23·4
86·8	753	23·1	46·7	39·2	28·0	14·2	51·8	262·2	457·3	1040	0·87	1·99	1·38	33·1	56·6	60·8	66·4	67·4	19·8
83·0	743	19·6	30·2	41·2	24·9	9·21	65·9	227·5	400·6	920	0·77	2·36	1·29	33·4	67·8	48·7	73·0	72·5	13·5
81·2	734·5	15·95	34·7	49·35	22·0	7·2	70·8	213	373	875	0·715	2·71	1·205	31·5	75·5	41·4	75·3	76·3	9·25
80·9	746·5	13·4	31·2	55·4	20·2	6·0	73·8	210	368·2	860	0·685	3·06	1·156	30·0	80·5	36·0	77·1	78·5	7·51
78·9	735	9·3	24·7	66·0	16·7	4·04	79·3	195	339·7	830	0·615	3·88	1·061	27·4	87·7	27·2	80·6	82·5	4·85
78·0	734·5	6·59	19·3	74·11	13·95	3·00	83·05	187·5	327·3	785	0·61	4·75	1·05	25·5	91·8	20·7	82·4	85·5	2·46
77·8	764·5	4·54	15·3	80·16	10·95	2·19	86·86	185	322	775	0·57	5·51	1·06	22·9	94·65	16·0	83·4	88·8	58·9

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Table 14 (*cont.*) *Ternary data. Water-acetic acid-ethyl acetate.*

Temp. (°C)	*Press.* (*mm*)	x_w	x_a	x_e	y_w	y_a	y_e	P_a	P_w	P_e	γ_a	γ_w	γ_e	*Liquid* $\frac{A}{A+W}$	$\frac{E}{E+W}$	$\frac{A}{A+E}$	*Vapour* $\frac{W}{A+W}$	$\frac{E}{E+W}$	$\frac{A}{A+E}$
98·2	764	57·5	39·4	3·11	60·7	23·1	16·2	392·5	712·4	1445	1·14	1·13	2·75	59·4	5·13	92·75	72·5	21·1	58·9
93·0	763	53·2	39·2	7·61	50·9	16·6	32·5	327·5	588·6	1240	0·988	1·24	2·63	57·6	12·5	84·0	75·4	39·0	33·8
96·45	757·5	11·2	66·5	22·3	17·9	35·6	46·5	370	669	1380	1·095	1·82	1·14	14·4	66·7	75·0	33·5	72·3	43·4
93·15	755	9·38	60·6	30·0	15·3	28·6	56·1	355	593	1250	1·06	2·074	1·13	13·4	76·3	67·0	34·8	78·8	33·8
91·2	750	8·3	57·0	34·7	14·0	23·7	62·3	307	550·2	1180	1·01	2·3	1·14	12·7	80·6	62·1	37·2	81·6	27·6
90·7	750	7·39	55·75	36·9	13·0	22·4	64·6	302	539·9	1160	0·998	2·44	1·13	11·7	83·3	60·2	36·7	83·3	35·7
86·8	740·5	14·0	49·4	36·6	19·9	16·4	63·7	262	465·1	1035	0·937	2·26	1·25	22·1	72·3	57·5	55·0	76·2	20·5
86·1	740·5	12·2	46·0	41·8	18·2	15·5	66·3	255	452·7	1010	0·978	2·45	1·160	20·9	77·5	52·5	54·0	78·5	19·0
84·35	738·5	9·86	41·0	49·1	15·7	11·7	72·6	240	423·6	960	0·874	2·78	1·135	19·4	83·3	45·5	57·4	82·3	13·8
83·9	738·5	8·35	39·2	52·5	14·1	10·8	75·1	235	415·2	950	0·855	2·98	1·105	17·6	86·3	43·0	56·8	84·3	12·5
82·1	734	6·25	33·2	60·6	11·9	7·46	80·6	220	386·5	895	0·75	3·62	1·09	15·9	90·7	38·4	61·5	87·2	8·5
81·2	735	5·0	28·9	66·1	10·0	6·15	83·9	214	372·7	870	0·73	3·92	1·07	14·8	93·0	31·4	62·0	89·4	6·83
80·0	745	3·43	21·1	75·4	7·84	3·94	88·2	202·5	355·1	840	0·685	4·8	1·04	14·0	96·1	21·9	66·6	91·9	4·27
78·9	743·5	2·4	15·7	81·9	6·49	2·36	91·1	194	339·1	810	0·576	5·92	1·02	13·3	97·2	18·1	73·4	93·4	2·53
99·7	749·5	23·4	67·9	8·7	32·7	40·0	27·3	–	–	–	–	–	–	24·8	–	88·6	45·0	–	59·5
96·6	750	21·2	64·0	14·8	29·1	34·1	36·8	373	67·2	1384	1·07	1·53	1·35	24·9	41·1	81·3	46·0	55·9	48·1
87·8	763	48·4	37·2	14·4	43 0	11·3	45·7	272·5	483	1065	0·851	1·4	2·27	56·5	22·95	72·1	79·3	51·5	19·8
82·1	753	39·8	32·5	27·7	36·0	6·925	57·1	221	386·4	895	0·726	1·76	1·73	55·0	41·0	54·0	84·0	61·3	10·8
78·8	755·5	30·9	26·6	42·5	32·0	4·35	63·65	193	338	806	0·64	2·31	1·4	53·75	58·0	38·5	88·0	66·5	6·4
77·4	755·5	24·55	22·8	52·75	28·2	2·72	69·08	182·5	319·3	770	0·495	2·72	1·285	54·0	68·5	30·2	91·2	70·5	3·79
76·0	750	17·0	17·2	65·8	24·2	2·45	73·36	172·5	301·4	733	0·618	3·54	1·14	49·8	79·5	20·7	90·9	75·2	3·21
75·6	750	12·55	13·15	74·3	20·8	2·05	77·15	167·5	296·6	720	0·698	4·19	1·081	48·9	85·6	15·05	91·0	78·8	2·59
75·7	754·5	8·7	11·1	80·2	16·25	1·69	82·06	170	297·8	725	0·677	4·74	1·065	44·0	90·3	12·15	90·6	83·5	2·02
103·25	756·4	12·6	76·5	10·9	20·8	51·7	27·5	470	862·5	1655	1·089	1·45	1·15	14·1	46·4	87·5	28·7	57·0	65·3
92·2	756·4	77·61	19·5	2·83	61·0	8·9	30·1	320	571·3	1210	1·078	1·04	6·65	80·0	3·52	87·3	87·3	33·0	22·8
99·8	748	27·98	63·6	8·42	37·35	37·4	25·25	415	754·6	1507	1·06	1·32	1·49	30·5	23·1	87·5	50·0	40·3	59·6
84·0	748	72·25	19·9	7·85	43·6	5·5	50·9	237·5	416·8	950	0·869	1·083	5·1	78·5	9·8	71·8	89·0	53·9	9·76
98·0	761·4	48·98	46·2	4·82	54·55	26·0	19·45	390	707·3	1438	1·098	1·20	2·14	51·5	8·99	90·5	67·8	26·3	57·25
78·8	766·3	64·75	18·15	17·1	34·6	3·1	62·3	192·5	–	805	0·68	1·20	3·47	78·1	20·9	51·5	92·0	64·4	4·75

The above equation applies strictly only to solutions in equilibrium with an ideal vapour mixture. The correction factors are uncertain for the acetic acid vapours due to the association of the acetic acid vapour, and are small for ethyl acetate and water, so no correction factors have been used.

The experimental results in Figs. 14, 15 and 16 are plotted by the method suggested by HANDS and NORMAN [36]. For a mixture of components A, B and C the procedure used is as follows. The ratio $\frac{100\,A}{A+B}$ in the vapour is plotted against the corresponding ratio $\frac{100\,A}{A+B}$ in the liquid, using the molal concentration of the third component C, as a parameter. Similar ratios of $\frac{100\,B}{B+C}$ and $\frac{100\,C}{A+C}$ in the liquid are plotted against ratios $\frac{100\,B}{B+C}$ and $\frac{100\,C}{A+C}$ in the vapour using the parameters A and B respectively. Figs. 17, 18 and 19 represent the log activity coefficients of A, B and C plotted against the mole percentage of A, B and C in the liquid with $\frac{100\,B}{B+C}$, $\frac{100\,A}{A+C}$, $\frac{100\,A}{A+B}$ used respectively as parameters. Lines of constant parameters were then interpolated between the experimental points as suggested by COLBURN and SCHOENBORN [5].

CORRELATION OF RESULTS

Methods for prediction of ternary data from binary data and for correlation of scanty ternary data, have been suggested by numerous authors [13], [38], [39], [40], and [41]. These methods of correlation and prediction may be classified into four main groups as follows :

(1) Linear interpolation.

(2) Volume fraction interpolation.

(3) Calculation of ternary activity coefficients by thermodynamically consistent two, three and four suffix equations, involving a number of constants calculated from binary data and, in some cases, ternary constants calculated from experimentally determined ternary data.

(4) The use of equations expressing ratios of the log activity coefficients (e.g., $\log \gamma_1/\gamma_2$, $\log \gamma_2/\gamma_3$, etc.) in terms of the mole percentages of each component in the liquid, and constants obtained from equations expressing the same ratios from the binary systems. This involves the use of ternary constants in certain cases.

In applying these methods to the irregular system ethyl acetate-acetic acid-water, we are concerned with the prediction of vapour liquid equilibria in both the miscible and immiscible ternary regions.

In the miscible ternary region the following difficulties arise.

(a) The correlation of the two binary systems in which acetic acid is one of the components becomes complicated by the association and inter-association effects which are possible with this component. In a ternary system it might be expected that there would be an even more irregular behaviour. As no really successful method has been found for the correlation of acetic acid-water the ternary results have been calculated using a molecular weight of 60 for acetic acid.

(b) Fig. 9, Part 3 *Chem. Eng. Sci.* 1954 **3** 48, shows that the binary system acetic acid-water cannot be correlated by the use of van Laar or Margules equations.

(c) Fig. 11, Part 3, *Chem. Eng. Sci.* 1954 **3** 48, shows that in the immiscible region of the system ethyl acetate-water, the van Laar equation does not hold. The equation is of the form $\log \gamma = \frac{K}{x}$. In a ternary mixture the mutual solubility of ethyl acetate and water is increased by the presence of acetic acid. The problem therefore arises as to whether or not in this increased miscible region the van Laar equation should be used for predicting ternary data.

From a consideration of the above points it is unlikely that equations of the type previously mentioned under groups (3) and (4) will be accurate, since if the ternary equations are to be applicable, the binary systems must obey binary equations of a similar form. It would thus appear

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that these methods may not be applicable to systems exhibiting partial miscibility or inter-association.

On the other hand, linear interpolation methods have the great advantage that it is not necessary for the binary data to be correlated by equations of similar form. Such methods are basically limited to certain symmetrical systems but it will be shown that by the introduction of a correction factor the method is applicable to irregular solutions.

From Figs. 4, 5 and 6 and from the data of PRATT [42] and work in our laboratories [43] it can be seen that linear interpolation does give a reasonable approximation to the experimental results. The accuracy of linear interpolation to irregular systems can be improved by the introduction of an appropriate correction factor.

The proposed equation is of the form

$$\log \gamma_1 = \left.\begin{aligned} &\frac{x_2}{x_2 + x_3}(\log_{12}\gamma_1) + \frac{x_3}{x_1 x_3}(\log_{13}\gamma_1) \\ &+ x_2 x_3 \left[\phi\, x_1 x_2 x_3\right] \end{aligned}\right\} \quad (4)$$

where $\log \gamma_1$ = log activity coefficient of component 1 in the ternary system at concentration x_1 in the liquid.

$\log_{12} \gamma_1$ = log activity coefficient of component 1 in the binary system 12 at some concentration of x_1 of component 1.

$\log_{13} \gamma_1$ = log activity coefficient of component 1 in the binary system 13 at some concentration x_1 of component 1.

Under certain conditions the final term of the above equation may become very small in which case linear interpolations between the binary systems will give a good approximation to actual behaviour.

Using a reduced form of the two suffix Margules equation and rearranging the equation, the following expression was obtained :

$$\begin{aligned} \log \gamma_1 = {} & \frac{x^2}{x_2 + x_3}\left[A_{12} + 2x_1(A_{21} - A_{12})\right](1-x_1)^2 \\ & + \frac{x_3}{x_2 + x_3}\left[A_{13} + 2x_1(A_{31} - A_{13})\right](1+x_1)^2 \\ & + x_2 x_3 \left[A_{21} - A_{12} - A_{32} - 2x_1 (A_{21} - A_{12}) + 2x_3 (A_{32} - A_{23}) - C(1-2x_1)\right] \quad (5) \end{aligned}$$

It will be noted that in this equation the terms $\left[A_{12} + 2x_1(A_{21} - A_{12})\right](1 - x_1)^2$ and $\left[A_{13} + 2x_1(A_{31} - A_{13})\right](1 - x_1)^2$ are the values of $\log \gamma_1$ in the binary systems at a concentration x_1 of component 1. These two terms in the above equation are therefore equivalent to the value given by linear interpolation between two binaries which obey the three suffix Margules binary equation. A similar analogy can be made for the 2 and 4 suffix Margules equations.

The assumption is now made that the final term is approximately of the same value even if the binary systems do not obey the Margules equation. The following equation is therefore proposed for irregular solutions such as ethyl acetate-acetic acid-water.

$$\begin{aligned} \log \gamma_1 = {} & \frac{x_2}{x_2 + x_3}\left[\log_{12}\gamma_1\right]_{x_1} \\ & + \frac{x_3}{x_2 + x_3}\left[\log_{13}\gamma_1\right]_{x_1} \\ & + x_2 x_3 \left[A_{21} - A_{12} - A_{32} - 2x_1(A_{21} - A_{12}) + 2x_3(A_{32} - A_{23}) - C(1-2x_1)\right] \quad (6) \end{aligned}$$

The constant C has to be obtained from ternary data, and in the system ethyl acetate-acetic acid-water, $C = 0$, has been used in equation (6).

COMPARISON OF METHODS

In Table 15 the values of activity coefficients predicted from binary data, using three different methods of prediction are compared with experimental ternary activity coefficient data (column 2)

Column 3 gives the results *for linear interpolation* using the activity coefficient plot, $\log \gamma = \frac{K}{x}$ for ethyl acetate-water in Fig. 11. If the van Laar correlation is used for ethyl acetate-water the discrepancy between the predicted and experimental results is greater.

Column 4 gives the predicted activity coefficient *for equation* (6) using the binary activity coefficient plot $\log \gamma = \frac{k}{x}$ in Fig. 11 and the activity coefficient plot for acetic acid-water in Fig. 9.

Column 5 gives the predicted activity coefficients based on *the three suffix Margules equation.*

Table 15. Water-acetic acid-ethyl acetate.

Liquid compositions			*Experimental results*			*Predicted by linear interpolation*			*Predicted from eq. (6) C = 0*			*Predicted from 3-suffix Margules eqns. C = 0*		
X_W	X_A	E	γ_W	γ_A	γ_E	γ_W	γ_A	γ_E	γ_W	γ_A	γ_E	γ_W	γ_A	γ_E
0·4	0·4	0·2	1·55	0·83	1·8	1·53	1·09	2·6	1·42	0·83	1·7	1·7	0·78	2·02
0·3	0·4	0·4	2·30	0·78	1·3	2·41	1·02	1·43	2·3	0·78	1·28	2·98	0·782	1·145
0·4	0·2	0·4	2·10	0·54	1·64	2·21	1·0	1·93	1·9	0·56	1·66	2·56	0·56	1·64
0·3	0·6	0·1	1·33	1·05	1·54	1·28	1·14	2·28	1·26	1·05	1·44	1·94	0·94	1·65
0·6	0·3	0·1	1·2	0·85	3·2	1·23	1·13	5·7	1·19	0·85	3·1	1·24	0·86	4·65
0·1	0·6	0·3	2·12	1·01	1·15	2·10	1·08	1·27	2·14	1·0	1·14	2·55	0·922	0·955
0·1	0·3	0·6	3·45	0·75	1·15	3·76	0·93	1·16	3·7	0·79	1·15	2·7	0·71	1·0

It will be seen that the values given by equation (6) are much nearer the experimental values than either of the other two methods. The results in column 4 calculated from equation (6) are shown to be within 5·0% of the experimental values.

It is interesting to note that in the increased miscible region (see 4 above under Correlation of Results) the closest agreement between predicted and experimental results is obtained by equation (6) and the $\log \gamma = \frac{K}{x}$ plot for ethyl acetate-water. This unexpected conclusion is being further investigated.

PREDICTION OF IMMISCIBLE VAPOUR LIQUID EQUILIBRIA

Only a limited amount of experimental work has been done in the equilibrium still when the ternary liquid mixture is immiscible. A new type of still is being designed in order to obtain further experimental data in this region.

It is suggested however that ternary vapour compositions in the immiscible ternary region can be predicted from equation (6) and the use of the equation $\log \gamma = \frac{K}{x}$ for the immiscible binary system. The vapour composition can be predicted either from liquid compositions based on an overall composition in the immiscible region or from ternary compositions on the solubility curve.

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The thermodynamics of solutions of non-electrolytes

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Abstract—The properties of an ideal solution are carefully reviewed, and their application to actual solutions of gases and liquids is considered. A number of general equations relating the properties of solutions of gases and liquids, both ideal and non-ideal, are developed.

Résumé—L'auteur fait avec soin la revue des fonctions caractéristiques d'une solution idéale et de leur application aux solutions réelles de gaz et de liquides.

Il expose des équations générales reliant les propriétés de gaz et de liquides idéaux ou non idéaux.

1. INTRODUCTION

THE concept of an ideal solution originated many years ago, and one might expect that the implication of the term would by now be quite clear to all who have studied thermodynamics. Unfortunately, this does not seem to be the case, at least among engineers. Thus, a careful re-examination of the ideal solution and its properties would seem to be justified. At the same time it is appropriate to consider the deviations of actual solutions from ideality. Engineers make use of such quantities as the volume change of mixing, the heat of mixing, the entropy change of mixing, etc. These quantities are related, though not in a simple way, and in theory at least they may all be calculated from experimental measurements of the volume change of mixing. The required relationships are derived below. This treatment will be limited to solutions of liquids and gases in which no dissociation or chemical reaction occurs.

Three conclusions are usually drawn from the statement that a solution is ideal :

(*a*) $\overline{V}_a = V_a$, $\overline{V}_b = V_b$, $\overline{V}_i = V_i$, etc., and therefore $\Delta V = 0$, as may be seen by comparing the equations :

$$V = z_a \overline{V}_a + z_b \overline{V}_b + \ldots + z_n \overline{V}_n \quad (1)$$

$$V = z_a V_a + z_b V_b + \ldots + z_n V_n + \Delta V \quad (2)$$

For gases this is equivalent to AMAGAT's law.

(*b*) $\overline{H}_a = H_a$, $H_b = H_b$, $\overline{H}_i = H_i$, etc., and therefore $\Delta H = 0$, as may be seen by comparing the equations :

$$H = z_a \overline{H}_a + z_b \overline{H}_b + \ldots + z_n \overline{H}_n \quad (3)$$

$$H = z_a H_a + z_b H_b + \ldots + z_n H_n + \Delta H \quad (4)$$

This is equivalent to the statement that the integral heat of mixing is zero.

(*c*) The Lewis and Randall rule is valid, i.e. :

$$\overline{f}_i = z_i f_i \quad (5)$$

Eqs. (1, 3) and (5) apply either to gaseous or liquid solutions, where all components are stable when pure in the same physical state as the solution at the temperature and pressure of the solution. Eqs. (2) and (4) are obviously completely general since ΔV and ΔH are defined so as to make them correct.

It is not my purpose to dispute these equations, for they certainly are correct for an ideal solution as originally defined. The original definition was clearly stated by LEWIS and RANDALL [2], who described an ideal solution as one in which the fugacity of each component is proportional to its mole fraction at all concentrations. This immediately leads to eq. (5), the Lewis and Randall rule. In addition, they stated that this proportionality, i.e., eq. (5), must hold at *all* temperatures and pressures. It is this part of

the definition which is sometimes overlooked. Indeed, it is not to be found in any of the standard textbooks on chemical engineering thermodynamics. The complete definition is usually repeated in textbooks on thermodynamics for chemists, but the necessity of the latter requirement is seldom made clear. More important, some explanation is required as to what is meant by *all* temperatures and pressures, particularly with regard to liquid solutions.

An incomplete understanding of the ideal solution has led some engineers, at least, to erroneous concepts. Notable among these is the notion that a solution is necessarily ideal, or nearly so, if at a given temperature and pressure its volume change on mixing is zero or small at all concentrations. That this is not so will be shown presently.

2. Derivation of General Equations

Let us now proceed to the development of general equations relating the quantities being discussed, starting with the relation between fugacity and volume. These derivations are for a *closed* system of constant mass and constant over-all or total composition. The system is not limited to a single phase, but may consist of both liquid and vapour. As a matter of convenience we will base all equations on one mole of material, so that the total amount of any component i will always be given by its mole fraction in the entire system, z_i.

By the first law of thermodynamics for a closed system,

$$dE = dQ - dW \tag{6}$$

For any reversible process in this closed system in which the only force is that of fluid pressure,

$$dQ = TdS \tag{7}$$

and

$$dW = pdV \tag{8}$$

Therefore,

$$dE = TdS - pdV \tag{9}$$

This equation relates properties only, and is therefore divorced from any consideration of the process causing the change even though a reversible process was assumed in arriving at it.

By definition,

$$F = E + pV - TS \tag{10}$$

and

$$dF = dE + pdV + Vdp - TdS - SdT$$

Substitution for dE by eq. (9), gives,

$$dF = Vdp - SdT \tag{11}$$

At constant temperature,

$$dF = Vdp \tag{12}$$

This familiar derivation has been repeated here to emphasize the fact that no limitations need be imposed concerning the number of components or phases. Thus F, E, V, and S refer to the total system, in this case one mole, regardless of its complexity. A consequence of eq. (11) is that p and T are always independent variables for F for any system whatever.

Eq. (12) may be written: $(\partial F/\partial p)_T = V$. Differentiating with respect to N_i, the number of moles of component i:

$$\left[\frac{\partial\,(\partial F/\partial p)}{\partial N_i}\right]_{T,p,z--} = (\partial V/\partial N_i)_{T,p,z--}$$

Where the symbol $z--$ indicates constant total composition. This may also be written:

$$\left[\frac{\partial\,(\partial F/\partial N_i)_{T,p,z--}}{\partial p}\right]_{T,z--} = (\partial V/\partial N_i)_{T,p,z--}$$

By the definition of a partial molal quantity this becomes:

$$(\partial \overline{F}_i/\partial p)_{T,z-} = \overline{V}_i$$

or, at constant temperature and composition,

$$d\overline{F}_i = \overline{V}_i\,dp \tag{13}$$

$\overline{F}_i$, the partial molal free energy of component i in solution, is also known as the chemical potential and is often given the symbol μ_i.

Again no assumption has been necessary as to the number or nature of the phases. Integration of this equation from p^*, the zero-pressure state, to p at constant temperature and composition, gives:

$$\overline{F}_i - \overline{F}_i^* = \int_{p^*}^{p} \overline{V}_i\,dp \tag{14}$$

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A further equality may be added to this equation through the definition of fugacity for a component in solution.
Thus :

$$\overline{F}_i - \overline{F}_i^\bullet = \int_{p^\bullet}^{p} \overline{V}_i \, dp = RT \cdot \ln (\overline{f}_i / z_i \, p^\bullet) \quad (15)$$

In a similar fashion eq. (12) may be integrated for pure component i at the same temperature and pressure, and combined with the defining equations for fugacity of a pure material, to give :

$$F_i - F_i^\bullet = \int_{p^\bullet}^{p} V_i \, dp = RT \cdot \ln (f_i / p^\bullet) \quad (16)$$

Subtraction of eq. (16) from eq. (15) gives :

$$\overline{F}_i - F_i - (\overline{F}_i^\bullet - F_i^\bullet) = \int_{p^\bullet}^{p} (\overline{V}_i - V_i) \, dp = RT \cdot \ln (\overline{f}_i / z_i f_i)$$

Since [1], $\overline{F}_i^\bullet - F_i^\bullet = RT \cdot \ln (z_i)$, the above equation becomes :

$$\overline{F}_i - F_i - RT \cdot \ln (z_i) = \int_{p^\bullet}^{p} (\overline{V}_i - V_i) \, dp = RT \cdot \ln (\overline{f}_i / z_i f_i) \quad (17)$$

It must be understood here that in the above equations corresponding values of $\overline{F}_i$ and F_i, $\overline{f}_i$ and f_i, and $\overline{V}_i$ and V_i are always taken at the same temperature and pressure *in their actual states* at these conditions even though the pure component may be in a different physical state than the mixture.

Eqs. (15, 16) and (17) are usually represented as applying only to single-phase systems ; however, such a limitation is not at all necessary, and indeed is incorrect. These equations are derived from the first law of thermodynamics together with the definitions of free energy and fugacity. The only assumptions required are that the system be closed and that the only force be that of fluid pressure. As seen from the derivations, no assumptions are necessary concerning the number or physical state of the phases either for a solution or for the pure components. Thus, integration may be carried through the two-phase region, and indeed must be, if these equations are applied to the liquid phase.

In connection with eq. (17) it should be pointed out that the group, $\overline{f}_i / z_i f_i$, is commonly called an activity coefficient and that its deviation from unity may usually be regarded as an indication of the deviation of the solution from ideality. Such an interpretation is correct only when $\overline{f}_i$ represents the fugacity of component i in a single-phase solution and f_i represents the fugacity of pure i in the same physical state as the solution at the temperature and pressure of the solution. For the latter, fictitious states are sometimes employed. In the integration of eq. (17), only actual states are used, and as a result the term, $\overline{f}_i / z_i f_i$, is properly regarded as an activity coefficient only for the single-phase regions at conditions such that the pure components can exist in stable form in the same state as the solution at the given temperature and pressure.

In eqs. (15, 16) and (17) the integrations are carried out at constant temperature, and constant over-all or total composition. The symbol, z_i, is used here to represent these over-all or total compositions so as to distinguish them in the two-phase region from the liquid and vapour compositions which are usually represented by x_i and y_i respectively. Of course, for a single phase z_i becomes identical with x_i or y_i, but in the two-phase region they are clearly different. It must be understood that while total composition is held constant for the integrations of eqs. (15) and (17), the phase compositions must vary in the two-phase region in accordance with the requirements of the phase rule since the temperature is also constant. In this connection a few general comments about the phase rule will not be amiss.

The only variables considered in this regard are temperature, pressure, and the individual phase concentrations. Total volume, total mass, total mass of any constituent, etc. are not phase-rule variables. When we speak of fixing the *state* of a system, we do not imply anything with respect to its size. Thus the phase rule may be used to predict what changes can be made in an *open* system without changing its state. But we are

here everywhere considering a *closed* system in which changes occur under restraints quite different from those in an open system. If we fix the total amounts of each constituent (as has been done by fixing the total composition and restricting the system to one mole of material), the only remaining variables are temperature and pressure, and fixing them determines all properties of the closed system provided that temperature and pressure can both vary, and vary independently. Thus we may write for such a system, $G = \phi(T, p)$ where G represents any property such as enthaply, entropy, or free energy. If temperature and pressure can not be varied or can not vary independently, then this relation fails. There is an exception to this, for if G is the free energy (F), then this relation is always valid because $F = \phi(T, p)$ under all circumstances as shown by eq. (11).

In the above equations, $\overline{V}_i$ and $\overline{F}_i$ are partial molal quantities, defined in the usual manner. These quantities are commonly thought of in connection with single phases, but they certainly have unique values for two-phase (or even multi-phase) systems at equilibrium, and the integration of eq. (17) through or into the two-phase region assumes the use of these quantities for the *total system* in the two-phase region. This point does not seem to have been discussed before, and therefore deserves elaboration. We have long been conditioned to think of fugacity and the partial molal quantities as applied only to single phases, but this is an unnecessary restriction. Consider the physical path analogous to the path of integration. We start with a vapour mixture of definite composition and definite amount at a pressure approaching zero, and compress at constant temperature and constant composition and constant amount of material. For each pressure the system will have a definite set of properties even after the dew point has been reached. Indeed, for any pressure between the dew point and the bubble point, there will be a definite division of the material between the two phases, and each phase will have a definite composition : x_a, x_b, etc. in the liquid and y_a, y_b, etc. in the vapour. Thus for each pressure all properties of the two-phase mixture are fixed, and volume, enthalpy, entropy, free energy, and the partial molal properties all have definite values. In the two-phase region the values of $\overline{f}_i$ and of $\overline{F}_i$ or μ_i must be the same for the liquid phase as for the vapour phase. Nothing about eq. (17) is contrary to this requirement. The equations developed in this paper do not in any way conflict with equations in common use, but rather supplement them.

Let us turn our attention now to the relation between the volume change which occurs on mixing and the integral heat of mixing. It has sometimes been assumed that these quantities are directly related, and that if one is zero or small, the other must also be zero or small. While this is by no means true, the two quantities are related, though not in any simple fashion. The equation relating them may be developed most directly as follows : (The derivation is for a binary mixture, but it may obviously be generalized for any number of components.) From eq. (4) :

$$\Delta H = H - z_a H_a - z_b H_b \qquad (18)$$

For a mixture [2],

$$H = H^\bullet + \int_{p^\bullet}^{p} [V - T(\partial V/\partial T)]\, dp \qquad (19)$$

Again the integration is carried out at constant temperature and total composition, and again the equation applies not only to the vapour, but also throughout the two-phase and liquid regions. The only requirement for the application of this equation to a closed system is that H be a function of both temperature and pressure. This can be true only when temperature and pressure are independently variable. In the case of a single phase, this is always true. For a two-phase system (the maximum we are considering here), temperature and pressure are not independently variable for a single component or for an azeotrope in multi-component systems. But for mixtures other than azeotropes, this equation is valid under all conditions in single- and two-phase systems. For azeotropes a latent-heat term would have to be added if the integration were carried through the two-phase region.

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While eq. (19) may be used in general to calculate enthalpies of both liquid and vapour mixtures, it can not be used as it stands to calculate the enthalpies of pure components in the liquid region. For a pure component, condensation at constant temperature also occurs at constant pressure, and the pressure and temperature are not therefore independent variables in the two-phase region. For this case a latent-heat term must be added to eq. (19) to take into account the enthalpy change caused by condensation at constant temperature and pressure. Thus we may write for the pure components, a and b:

$$H_a = H_a^\bullet + \int_{p^\bullet}^{p} [V_a - T(\partial V_a/\partial T)]\, dp - L_a \quad (20a)$$

$$H_b = H_b^\bullet + \int_{p^\bullet}^{p} [V_b - T(\partial V_b/\partial T)]\, dp - L_b \quad (20b)$$

L_a and L_b are the molal latent heats of pure a and pure b at the temperature of the mixture. Eqs. (20a) and (20b) are written specifically for the liquid phase, but they are valid for the vapour phase if the latent-heat terms are omitted.

Substitution of eqs. (19), (20a), and (20b) in eq. (18) gives:

$$\Delta H = H^\bullet - z_a H_a^\bullet + z_a L_a - z_b H_b^\bullet + z_b L_b + \int_{p^\bullet}^{p} \left[V - z_a V_a - z_b V_b - T\left(\frac{\partial V}{\partial T}\right) + z_a T\left(\frac{\partial V_a}{\partial T}\right) + z_b T\left(\frac{\partial V_b}{\partial T}\right)\right] dp$$

But by eq. (2), $V - z_a V_a - z_b V_b = \Delta V$, and $-(\partial V/\partial T) + z_a(\partial V_a/\partial T) + z_b(\partial V_b/\partial T) = -(\partial \Delta V/\partial T)$.

Therefore,

$$\Delta H = \int_{p^\bullet}^{p} \left[\Delta V - T\left(\frac{\partial \Delta V}{\partial T}\right)\right] dp + H^\bullet - z_a H_a^\bullet - z_b H_b^\bullet + z_a L_a + z_b L_b.$$

But by eq. (4),

$$H^\bullet - z_a H_a^\bullet - z_b H_b^\bullet = \Delta H^\bullet$$

However, $\Delta H^\bullet$, the integral heat of mixing at $p^\bullet$, approaches zero for a value of $p^\bullet$ approaching zero.

Therefore,

$$\Delta H = \int_{p^\bullet}^{p} [\Delta V - T(\partial \Delta V/\partial T)]\, dp + z_a L_a + z_b L_b$$

Generalizing,

$$\Delta H = \int_{p^\bullet}^{p} [\Delta V - T(\partial \Delta V/\partial T)]\, dp + \Sigma(z_i L_i) \quad (21)$$

As it stands, eq. (21) gives the relationship between the integral heat of mixing and the volume change of mixing for liquid mixtures. If the latent-heat terms are omitted, it applies to gas mixtures. Clearly, the heat of mixing depends not only on the volume change of mixing at the temperature and pressure of mixing but on the volume changes at all lower pressures as well. The integral in eq. (21) is evaluated at constant temperature and total composition. It should be emphasized that for a liquid mixture this integration must be carried through the two-phase region and that ΔV always represents the difference between the mixture volume and the volumes of the pure components *in their actual states* at the temperature and pressure of the mixture even though these states may be different. Of course, ΔV will ordinarily be finite for actual gases at a pressure approaching zero even though the ideal-gas law is valid at this pressure.

We can now complete the picture by deriving several more relationships between the Δ's of mixing for solutions of both gases and liquids. By eq. (17) (constant temperature and composition):

$$\bar{F}_i - F_i - RT \cdot \ln(z_i) = \int_{p^\bullet}^{p} (\bar{V}_i - V_i)\, dp$$

But

$$\bar{F}_i = \bar{H}_i - T\bar{S}_i \quad \text{and} \quad F_i = H_i - TS_i$$

Therefore

$$\bar{H}_i - T\bar{S}_i - H_i + TS_i - RT \cdot \ln(z_i) = \int_{p^\bullet}^{p} (\bar{V}_i - V_i)\, dp$$

Multiplying through by z_i and summing over all components :

$$\Sigma(z_i\overline{H}_i) - \Sigma(z_iH_i) - T\,\Sigma(z_i\overline{S}_i) + T\,\Sigma(z_iS_i) - RT\,\Sigma(z_i \ln z_i) = \int_{p^\circ}^{p} [\Sigma(z_i\overline{V}_i) - \Sigma(z_iV_i)]\,dp$$

By the definitions of ΔH, ΔS, and ΔV, this reduces to :

$$\Delta H - T\Delta S - RT\,\Sigma(z_i \ln z_i) = \int_{p^\circ}^{p} (\Delta V)\,dp$$

But at constant temperature, $\Delta H - T\Delta S = \Delta F$. Therefore

$$\Delta F = \int_{p^\circ}^{p} (\Delta V)\,dp + RT\,\Sigma(z_i \ln z_i) \qquad (22)$$

By the definition of the excess free energy of mixing, i.e., the free energy change over and above that for mixing ideal gases,

$$\Delta F_{xs} = \Delta F - RT\,\Sigma(z_i \ln z_i)$$

Therefore

$$\Delta F_{xs} = \int_{p^\circ}^{p} (\Delta V)\,dp \qquad (23)$$

Since $\Delta S = (\Delta H - \Delta F)/T$, then by eqs. (21) and (22) :

$$\Delta S = -\int_{p^\circ}^{p} (\partial \Delta V/\partial T)\,dp - R\,\Sigma(z_i \ln z_i) + \Sigma(z_i L_i)/T \qquad (24)$$

By the definition of the excess entropy of mixing, i.e., the entropy change over and above that for mixing ideal gases,

$$\Delta S_{xs} = \Delta S + R\,\Sigma(z_i \ln z_i)$$

Therefore

$$\Delta S_{xs} = -\int_{p^\circ}^{p} (\partial \Delta V/\partial T)\,dp + \Sigma(z_i L_i)/T \qquad (25)$$

Eqs. (24) and (25) as written apply to liquid solutions. For a gaseous mixture the latent-heat term must be omitted. The integrals in these equations are, of course, evaluated at constant temperature and total composition.

3. Application of the General Equations to Ideal Solutions

The equations developed above are general relations applying alike to ideal and non-ideal solutions. For the case of the ideal solution, however, they may be greatly simplified.

Let us apply eq. (17) to the case of an ideal solution as defined by Lewis and Randall. For such a solution, $\overline{f}_i = z_i f_i$; therefore $\ln(\overline{f}_i/z_i f_i) = 0$, and eq. (17) reduces to :

$$\overline{F}_i - F_i = RT \cdot \ln(z_i) \qquad (26)$$

This equation is a general relation for a given solution only if true over a range of temperatures and pressures. This accounts for the requirement that $\overline{f}_i = z_i f_i$ for an ideal solution at all temperatures and pressures, for we are about to differentiate eq. (26) first with respect to pressure and then with respect to temperature, and such differentiations would not be admissible were this not a general equation. For an ideal solution as originally defined, it is completely general, as are the equations which result when it is differentiated. The requirement that the Lewis and Randall rule holds at *all* temperatures and pressures obviously restricts consideration to a hypothetical solution in which no phase changes occur.

Differentiation of eq. (26) with respect to pressure gives :

$$(\partial \overline{F}_i/\partial p) - (\partial F_i/\partial p) = 0$$

Therefore [1] : $\overline{V}_i = V_i$ and $\Delta V = 0$ for an ideal solution.

Dividing eq. (26) by T and differentiating with respect to temperature gives :

$$\frac{\partial(\overline{F}_i/T)}{\partial T} - \frac{\partial(F_i/T)}{\partial T} = 0$$

Therefore [1] : $-\overline{H}_i/T^2 + H_i/T^2 = 0$. Thus $\overline{H}_i = H_i$ and $\Delta H = 0$ for an ideal solution. The same conclusion is reached by substituting $\Delta V = 0$ into eq. (21) and noting that this must hold at all temperatures and pressures. Since this can be true only if no phase change is involved, the latent-heat term must be omitted. In the same way, eqs. (23) and (25) may be used

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to show that ΔF_{xs} and ΔS_{xs} are zero for ideal solutions.

It should be clear from the above discusson that an ideal solution may be defined equally well by stating that it has any one of the three attributes listed at the beginning of this paper, provided that this attribute is stated to hold at all pressures, temperatures, and concentrations. This is all very satisfying from the mathematical point of view, but the engineer is interested in using these relations, as approximations at least, for real solutions, and no real solution can be ideal at *all* temperatures and pressures. The practical problem then is one of determing when or over what range of conditions these equations, true for ideal solutions, may be used as good approximations for real solutions.

4. Application of General Equations to Non-Ideal Solutions

Consider now a few general cases of non-ideal behaviour. They will be represented by diagrams of $(\bar{V}_i - V_i)$ vs. pressure at constant composition with temperature as parameter. The first three cases will deal with gases only, and we will start with the relatively simple case represented in Fig. 1. This situation is purely hypothetical, and probably does not actually exist. According to eq. (17),

$$RT \cdot \ln (\bar{f}_i / z_i f_i) = \int_{p^\circ}^{p} (\bar{V}_i - V_i)\, dp$$

Therefore $\bar{f}_i$ will equal $z_i f_i$ at all pressures up to the point where $\bar{V}_i$ is no longer equal to V_i along an isotherm. Furthermore, $\bar{H}_i$ will equal H_i up to nearly the same pressure. This case represents a situation where a solution could be ideal for all practical purposes over a limited range of conditions.

Fig. 1. Schematic diagram. Constant total composition.

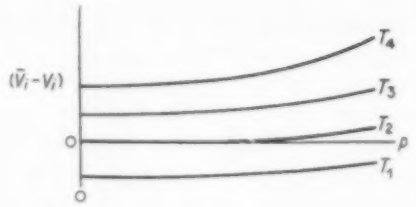

Fig. 2. Schematic diagram. Constant total composition.

In the situation represented by Fig. 2, no ideal solution is possible. Again, this is a hypothetical situation which may or may not actually exist. It is true that at the temperature T_2, $(\bar{V}_i - V_i) = 0$ for a range of pressures down to zero, and that $\bar{f}_i = z_i f_i$ over this pressure range, but $\bar{H}_i$ is never equal to H_i over this pressure range. This may be seen by differentiating eq. (17) with respect to temperature after having first divided through by T. The differentiation is carried out at constant pressure and composition, and gives :

$$\bar{H}_i - H_i = \int_{p^\circ}^{p} (\bar{V}_i - V_i)\, dp - (T) \frac{\partial \int_{p^\circ}^{p} (\bar{V}_i - V_i)\, dp}{\partial T} \qquad (27)$$

While the first term on the right-hand side of this equation is zero over a wide range of pressures at T_2, the second term will always have a value. Thus such a solution may act as an ideal solution at this temperature in certain respects, but not in all respects, and therefore cannot be called an ideal solution.

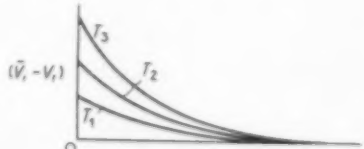

Fig. 3. Schematic diagram. Constant total composition.

The situation represented in Fig. 3 is commonly encountered with gaseous solutions at temperatures above the critical. Experimental evidence shows that some if not all gas mixtures very nearly obey Amagat's law at high pressures (usually above several hundred atmospheres), even though

at lower pressures, indeed at zero pressure, this lay may fail. In such a case the Lewis and Randall rule is never exactly valid for any temperature shown, for the integral term of eq. (17) always has a value even in the region where $\overline{V}_i = V_i$. Moreover, $\overline{H}_i$ does not become equal to H_i in this region because the value of the integral is different for different temperatures. However, the ratio, $\overline{f}_i/z_i f_i$, becomes constant at high pressures for a given temperature, and the difference between $\overline{H}_i$ and H_i becomes constant for the same conditions. This is apparent from eqs. (17) and (27).

Of the three general cases considered above for gases, only the first represents a behaiour suitable for the exact application of the equations for an ideal solution over any finite range. Unfortunately, this is strictly a hypothetical behaviour, not known to be exhibited by any actual gas mixture. This analysis lends support to the view expressed by REDLICH and KWONG [3] that no gaseous mixture can behave as an ideal solution unless it is also an ideal gas. This does not mean that the use of the equations for an ideal solution cannot represent any improvement over the use of the equations for an ideal gas, for while neither may be correct as applied to actual gases, the former certainly may be much more nearly so than the latter.

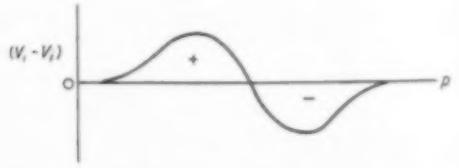

FIG. 4. Schematic diagram. Constant total composition

The general case represented by Fig. 4 is particularly important, for it includes the situation which must exist for any ideal *liquid* solution. If one starts with a vapour mixture at the very low pressure, p^*, and compresses at a constant temperature below the critical temperature, the dew point will eventually be reached. Further compression results in continued liquefaction until the bubble point is reached. While it is perhaps possible for $\overline{V}_i$ to equal V_i in the single-phase regions, this cannot be the case in the two-phase region.

Consider now a plot of V, the total volume, vs. z_a for a two-component mixture consisting of a and b, with a being the more volatile, at a temperature and pressure such that pure b is a liquid and pure a is a vapour. Such a plot is shown in Fig. 5. It should be emphasized again

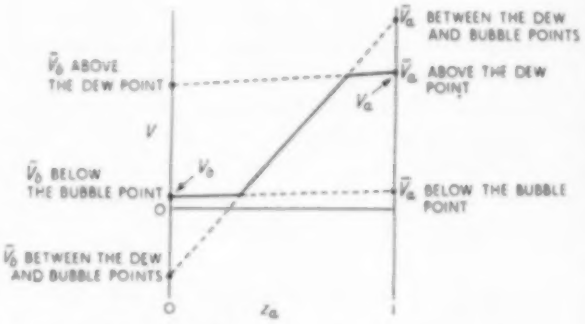

FIG. 5. Volume vs. mole fraction. Constant temperature and pressure.

that V and z refer to the entire mixture even in the two-phase region. From this diagram, using the method of tangent intercepts [2], we can determine the relative values that $\overline{V}_a$ and $\overline{V}_b$ must have. Using this information, we can prepare a graph of total volume, pure-component volumes, and partial molal volumes as a function of pressure for this same binary mixture at constant temperature and total composition. This is shown in Fig. 6.

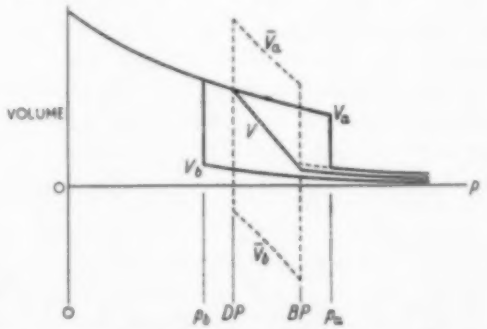

FIG. 6. Mixture volume, pure component volumes, and partial molal volumes vs. pressure. Constant temperature and total composition.

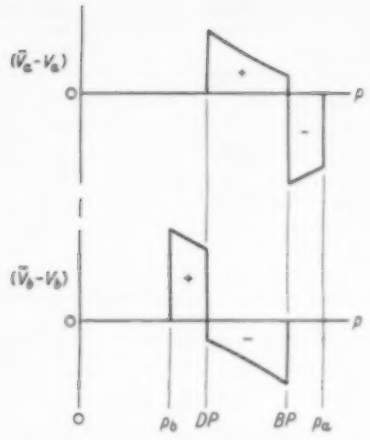

FIG. 7. Schematic diagram. Temperature and total composition constant.

From the values given by Fig. 6, graphs of $(\bar{V}_a - V_a)$ and $(\bar{V}_b - V_b)$ vs. pressure can be drawn. These are shown in Fig. 7. Temperature and total composition are constant. The curves shown are of the shape obtained when RAOULT's law is assumed for the vapour-liquid equilibrium relation. In addition additivity of volumes in the single-phase regions has been assumed. Thus, we have represented here the simplest possible case. Clearly it is not possible for $(\bar{V}_i - V_i)$ to be zero at all pressures from zero to the pressure in question for a liquid mixture. However, it is possible for the plus areas to be equal to the minus areas in Figs. 4 or 7, and therefore for the integral term of eq. (17) to be zero in the liquid region. If this is the case, the liquid may well be an ideal solution. The only additional requirement is that this be true not only at the temperature in question but over a range of temperatures including the temperature in question; otherwise the heat of mixing would not be zero as can be seen from eq. (27).

It is also possible, of course, for the plus area to be greater or less than the minus area, and still have a liquid solution for which $\bar{V}_i = V_i$. Such a solution could not be ideal, since the integral term in eq. (17) would not be zero, and therefore the Lewis and Randall rule would not be true. Furthermore, in such a case one could hardly expect the value of this integral to be the same over a range of temperatures even though the liquid volumes remained additive, and therefore the heats of mixing could not be zero. Such a situation is given a generalized representation in Fig. 8.

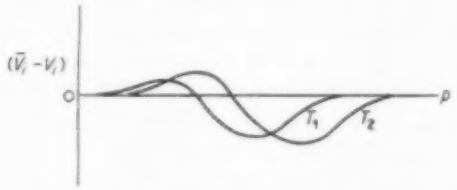

FIG. 8. Schematic diagram. Total composition constant.

There are undoubtedly examples of actual liquid solutions for which the volume change of mixing is very small over a wide temperature range, but which are by no means ideal from the standpoint of the Lewis and Randall rule or of zero or small heats of mixing. The existence of such solutions is easily explained on the basis that their vapour-liquid equilibrium relation is such as to give a finite value to the integral term of eq. (17) through the two-phase region. As a matter of fact, the volume changes which occur from the mixing of liquids are almost always small relative to the volume changes which result when mixtures in the two-phase region are formed. Thus, it is the nature of the vapour-liquid equilibrium relationship which is of major importance in determining the magnitude of the heat of mixing and the deviation of the activity coefficients $(\bar{f}_i/x_i f_i)$ from unity for liquid solutions.

This raises the question of what the vapour-liquid equilibrium relationship must be in order that a liquid be an ideal solution. No completely general answer to this question seems to be possible; however, if the vapour phase is assumed to be an ideal gas, the required relation is very nearly RAOULT's law, and if one assumes pressure to be without effect on the vapour pressures of the pure components, it is exactly RAOULT's law. Clearly, there are many vapour-liquid equilibrium relationships which could lead to the situation shown in Fig. 7, where the plus and minus areas are equal. The conclusion which must be drawn from this observation is that RAOULT's law cannot be derived from the simple

assumptions that the liquid volumes are additive and that the vapour is an ideal gas. The necessary assumptions are, that the integral term of eq. (17) be zero, and that the vapour be an ideal gas.

We have been considering the application of eq. (17) to the entire system as we have defined it. This equation reduces to the Lewis and Randall rule for a given component eq. (5) only when the integral term is zero. This cannot be the case in the two-phase region as can be seen by examining Fig. 7. Thus, one cannot apply the Lewis and Randall rule to the system as a whole if the system consists of two phases. One can, however, apply eq. (17), and thus the Lewis and Randall rule where it is warranted to the individual phases. This often requires the use of fictitious states for the pure components, for as can be seen from Fig. 7, the integral term in eq. (17) cannot be zero in a limited region outside the two-phase region when only actual states are employed. To avoid this difficulty outside the two-phase region, it is customary to use values of f_i in the Lewis and Randall rule for the pure components in the state (liquid or vapour) in which the solution exists, even though the pure component does not actually exist in this state. In such cases the Lewis and Randall rule is written $\bar{f}_i = x_i f_i$ or $\bar{f}_i = y_i f_i$ depending on whether the phase being considered is liquid or vapour. In the equations derived in this paper, the use of fictitious states has been avoided. However, this is not to say that there is anything objectionable about their usual and proper use.

The application of eq. (21) to liquid solutions is also of interest. The latent-heat terms are, of course, large. For an ideal solution ΔH is zero, and even for non-ideal solutions ΔH is often relatively small. Thus the integral term must have a large value. This comes largely from the two-phase region, which must be passed in reaching the liquid state from the zero-pressure state. Thus, ΔH depends on the difference between two relatively large numbers. Representative values of ΔH and ΔV for liquids at about 20°C as given by SCHMIDT [4] are listed in Table 1. In each case values are for an equimolal mixture. The units are cal/gm of solution for ΔH and cc/gm of solution for ΔV.

Table 1. *Representative values of* ΔH and ΔV.

System	ΔH	ΔV
Acetone-Carbon disulphide	+ 5·00	+ 0·0140
Acetone-Chloroform	− 5·56	− 0·0020
Benzene-Methyl alcohol	+ 1·98	− 0·0014
Benzene-Carbon disulphide	+ 1·90	+ 0·0095
Benzene-Ethyl ether	0·00	− 0·0060
Benzene-Carbon tetrachloride	+ 0·25	+ 0·0051
Benzene-Propyl alcohol	+ 2·93	− 0·0052
Carbon disulphide-Carbon tetrachloride	+ 1·59	+ 0·0053

These data show clearly that there is no direct relationship between ΔH and ΔV. However, eq. (21) is in accord with such results as is eq. (27). Whether or not eq. (21) could be used to advantage for the calculation of heats of mixing of liquids is questionable. Certainly, very accurate volume measurements would be required not only in the vapour region but in the two-phase region as well. Of course, such measurements are being made in the vapour region, but one has the added difficulty of assuring phase equilibrium if they are extended into the two-phase region. On the other hand, the direct determination of accurate heats of mixing is also quite difficult.

We may conclude from this discussion that one must be careful not to assume a liquid solution to be ideal or nearly so in all respects just because it shows negligible or small volume changes of mixing in all concentrations, even over a wide range of temperatures, for this can be true even though the Lewis and Randall rule is not valid, and the heat of mixing not zero. To test a liquid solution for approach to ideality, one should measure not only volume changes of mixing over a range of concentration and temperature, but also heats of mixing (or temperature changes of mixing).

This paper has dealt only with purely thermodynamic relationships, and has not been concerned with the question of ideality from the standpoint of molecular structure and intermolecular forces. While it should be possible to determine the approach to ideality of a solution on its own merits in this way, present knowledge does not in general permit it. Thus one must have recourse to thermodynamic relationships such as are presented here.

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Acknowledgement—The constructive criticisms and suggestions of Professor R. H. BRETTON of Yale University in reviewing this paper are gratefully acknowledged.

NOTATION

F_i = molal free energy of pure component i at the temperature and pressure of the solution
$\overline{F}_i$ = partial molal free energy of component i in solution; same as the chemical potential, μ_i.
ΔF = free energy change of mixing at constant temperature and pressure to form 1 mole of solution
ΔF_{xs} = free energy change of mixing over and above that for the mixing of ideal gases
f_i = fugacity of pure component i at the temperature and pressure of the solution
$\overline{f}_i$ = fugacity of component i in solution
H = molal enthalpy of the solution
H_i = molal enthalpy of pure component i at the temperature and pressure of the solution
$\overline{H}_i$ = partial molal enthalpy of component i in solution
ΔH = enthalpy change of mixing at constant temperature and pressure to form 1 mole of solution (integral heat of mixing)
L_a, L_b = molal latent heats of pure a and pure b at the temperature of the solution
p = pressure
R = universal gas constant
S_i = molal entropy of pure component i at the temperature and pressure of the solution
$\overline{S}_i$ = partial molal entropy of component i in solution
ΔS = entropy change of mixing at constant temperature and pressure to form 1 mole of solution
ΔS_{xs} = entropy change of mixing over and above that for the mixing of ideal gases
T = absolute temperature
V = molal volume of the solution
V_i = molal volume of pure component i at the temperature and pressure of the solution
$\overline{V}_i$ = partial molal volume of component i in solution
ΔV = volume change of mixing at constant temperature and pressure to form 1 mole of solution
x_i = mole fraction of component i in a liquid phase
y_i = mole fraction of component i in a vapour phase
z_i = mole fraction of component i in the total system, whether vapour, liquid, or a combination of both
$^\bullet$ = a superscript, designating the zero-pressure state

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Letters to the Editors

The mechanism of mass transfer of solutes across liquid—liquid interfaces

THE two recent papers by J. B. LEWIS [2, 3] report data on mass transfer across the flat interface between two immiscible liquids in a stirred vessel. There appear to be several reasons to question the conclusion that mass transfer in such a system "takes place by eddy and *not* molecular diffusion," a conclusion which is at variance with current theory.

The common picture of the mechanism of mass transfer to a phase boundary is one of transport by eddy motion in the flowing or agitated bulk of the fluid, with eddy motion in a direction normal to the surface damped out near the surface. Lack of perpendicular velocity components, resulting from this damping, suggest that in the limit, as the surface is approached, molecular motion is the only possible mechanism of mass transfer. It is difficult to see how lateral motion of the surface, as in the case of two stirred immiscible liquids, would change this picture.

Molecular diffusion is notoriously slow as compared with eddy diffusion, and the effect of the molecular diffusion coefficient D is not significant in the stirred bulk of the fluid. As the surface is approached the rate of transfer should, in the limit, be proportional to D. It may be expected, then, that the over-all process will be proportional to D raised to some power between zero and unity. Empirical correlations of mass transfer data frequently involve D^n, where n is in the vicinity of 0·5. Variations in turbulence affect both eddy transport and the effective thickness of the region near the surface where D is of importance, so GILLILAND [1], for example, found no evident variation of n as the stream velocity was varied several fold. The Danckwerts surface-renewal model, likewise, calls for a constant value of n of 0·5.

Because of the large number of variables involved, LEWIS' task of correlating his extensive data was admittedly difficult, but it was not made easier by the fact that his results were not reproducible.

In a number of cases the values of the mass transfer coefficient k differed by more than two-fold in presumably identical tests. In spite of the fact that smoothed data were used, the final correlation (Fig. 4 of the first paper) shows a wide spatter of points, and the furfural data lie more than 100 per cent above the best line. The resulting correlation is curious in that the viscosity of the "other phase" cancels. Over a wide range the line of Fig. 4 has a slope of nearly unity so that the viscosity of the phase under consideration also cancels. The result, roughly, is a correlation of k with stirrer speeds.

Under the circumstances, it is not unreasonable to believe that other methods of correlation might serve equally well, and that a correlation involving D might have been obtained. Too few reliable values of D are available to attempt this properly, but the possibility can de demonstrated.

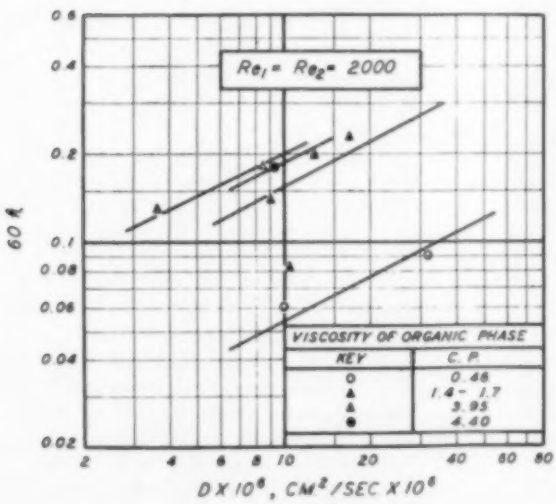

FIG. 1

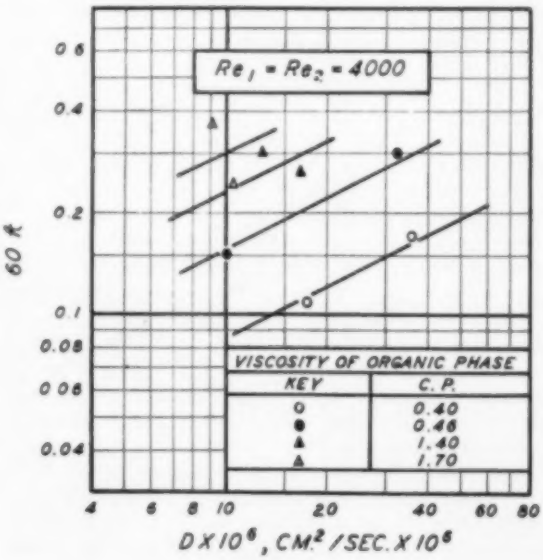

FIG. 2

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Replotting the original data in the manner of LEWIS, Fig. 3, values of k were interpolated for Reynolds numbers in both phases of 2,000 and 4,000. This smoothing procedure is quite uncertain, but a few values good to perhaps 30 per cent were obtained for those systems for which LEWIS reports [4] values of D. These are shown on the accompanying logarithmic graphs (Figs. 1 and 2) as k vs. D, with lines of slope 0·5 sketched in. This fragmentary correlation does not, at least, do violence to the idea that k depends in some way on D, and it would not be unreasonable to conclude that k is proportional to the square root of D, as found by other workers. The coefficient k appears to increase regularly with the viscosity of the organic phase, though the values of k shown are for diffusion in both organic and aqueous phase. Perhaps the more viscous organic liquids caused increased shear at the interface, with a resulting increase in k in each phase, quite apart from the effect of Reynolds number. It cannot be claimed that this approach to a correlation is comprehensive or even valid-only that one involving D cannot be ruled out, and that LEWIS' conclusion that molecular diffusion plays no part must be questioned.

If the correlation presented in the first paper is suspect, then the analysis of the data of the second paper dealing with mass transfer of a third component, is even more questionable. Quite apart from the possibility of other correlation procedures, it would seem that the poor reproducibility of the data and the deviations of experimental k's from LEWIS' general correlation would throw serious doubt on the reliability of the calculated values of k_{rw}, and perhaps even of the existence of a "slow interfacial reaction."

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In reply to Professor Sherwood

ALTHOUGH the presence of a laminar boundary layer at solid-liquid interfaces has been conclusively demonstrated experimental difficulties have hitherto prevented the direct investigation of flow patterns at gas-liquid and liquid-liquid interfaces. Nevertheless it is commonly postulated, from analogy with the solid-liquid surface, that similar boundary layers are always obtained, under all stirring conditions, at these interfaces also. This postulate has been accepted as correct because it is possible to correlate experimental data on the basis of a molecular diffusional process being the rate controlling step. It is not at all clear why this postulate, which assumes zero perpendicular velocity at gas-liquid and liquid-liquid interfaces, arose since in these cases there is no rigid immobile surface as at the solid-liquid bondary. Again it has recently been shown by DANCKWERTS [1], in connection with gas absorption, that different transport mechanisms will nevertheless all lead to transfer equations of essentially the same form. Although KISHINEVSKII [2] has criticised DANCKWERTS' own postulated mechanism and has shown that absorption could well be entirely turbulence controlled he again derives a transfer equation of the customary type. Thus it is clear that ability to correlate experimental data according to an equation derived from a diffusional layer theory is in itself no proof of the validity of the theory.

In my work the most direct evidence for the absence of laminar boundary layers, *under the particular stirring conditions used*, was that the transfer coefficients were independent of the relative directions of rotation of the two stirrers. Most experiments were carried out with contra-rotating stirrers, to produce maximum shear near the interface, which was then always disturbed by small ripples. In 10 experiments both stirrers were rotated in the same direction giving a very smooth interface with minimum shear but there was no significant difference in the transfer coefficients. It was possible to start an experiment with contra-rotating stirrers and to reverse one stirrer midway through the experiment without a break appearing in the (linear) plot of log $(c_\infty - c)$ versus time Clearly if laminar layers had been present they could not have been of the same thickness in the two cases. On the other hand if transfer was by eddy diffusion the important factor would be the component of velocity perpendicular to the interface, which would be independent of the direction of stirring.

A further check on the validity of a diffusional process was made by measuring transfer rates at different temperatures. At 50° it was clear, in spite of the experimental scatter, that there was not the large increase in transfer rate to be expected if the rates were diffusion controlled. Again the much greater retardation produced by rigid interfacial films on the transfer rate, as compared with mobile films, can be explained by the assumption that in the former case the rigid interface allows laminar layers to be built up whereas the mobile film has no effect.

The scatter of results in Fig. 4 arises mainly from the somewhat different coefficients observed at similar values of the group $(Re_1 + Re_2\,\eta_2/\eta_1)$ which were however obtained from different combinations of the two Reynolds numbers. This scatter is much less when the two Reynolds numbers are equal. An idea of the average experimental scatter can be obtained from the data plotted in Fig. 3.

It is clear that there is at least one further term missing from the correlation but provided the two Reynolds numbers are approximately equal then the data can be predicted to sufficient accuracy by the existing graph. The experiments reported in Part II were carried out as far as possible with the two Reynolds numbers equal.

The criticism that over a wide range of Fig 4, the two viscosities both cancel is hardly valid since this merely demonstrates once again that the process is turbulence controlled.

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ANNOUNCEMENT

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Prospective contributors are requested to submit the titles and a two-hundred-word abstract for their papers not later than January 1, 1956. The full paper must be ready for preprinting by March 1, 1956. All papers submitted for presentation at the Congress will be reviewed by a committee before acceptance.

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